2018

Life cycle assessment (LCA) and techno-cconomic analysis (TEA) of biobased adhesive derived from glycerol

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Life Cycle Assessment (LCA) and Techno-Economic Analysis (TEA) of biobased adhesive derived from glycerol

by

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A dissertation submitted to the graduate faculty

in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Major: Agricultural and Biosystems Engineering

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The student author, whose presentation of the scholarship herein was approved by the program of study committee, is solely responsible for the content of this dissertation. The Graduate College will ensure this dissertation is globally accessible and will not permit alterations after a degree is conferred.

Iowa State University

Ames, Iowa

2018

DEDICATION

This dissertation is dedicated to my parents for their endless love and support. Thank you for always being there for me!

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NOMENCLATURE

AIBN	Azobisisobutyronitrile
AOC	Annual Operating Cost
AP	Acidification Potential
ASTM	American Society for Testing and Materials
CTA	Chain Transfer Agent
DCF	Discount Cash Flow
EI	Eco-Indicator
EIO	Economic Input and Output
EP	Eutrophication Potential
FU	Functional Unit
GHG	Greenhouse Gas
GREET	Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation
GWP	Global Warming Potential
ISO	International Organization for Standardization
LCA	Life Cycle Assessment
LCI	Life Cycle Inventory
MDF	Medium Density Fiberboard
MO	Metal Oxide
MSP	Minimum Selling Price

MUF	Melamine Urea Formaldehyde
NREL	National Renewable Energy Laboratory
NPV	Net Present Value
ODP	Ozone Depletion Potential
PAG	Poly-acrylated Glycerol
PEL	Permissible Exposure Limit
PF	Phenol Formaldehyde
PRF	Phenol Resorcinol Formaldehyde
PSA	Pressure Sensitive Adhesive
PVC	Polyvinyl Alcohol
RAFT	Reversible Addition-Fragmentation chain Transfer
ROI	Return on Investment
TCI	Total Capital Investment
TEA	Techno-Economic Analysis
TRACI	Tool for Reduction and Assessment of Chemicals and Other Environmental Impacts
UF	Urea Formaldehyde
U.S. EIA	U.S. Energy Information Administration
USDA	U.S. Department of Agriculture
U.S. EPA	U.S. Environmental Protection Agency
VOC	Volatile Organic Compound

ACKNOWLEDGMENTS

Looking back into the six years since I came to Iowa State University, I just realized how fortunate I am with the support of so many people. First of all, I would like to express my sincere gratitude to my major professor, Dr. Kurt Rosentrater. Thank you for trusting me in charge of the bio-adhesive modeling project. Your guidance, suggestions and encouragement on this project helped me becoming more creative and open-minded that help me successfully complete this project. More importantly, thank you for encouraging me to pursue my dreams when I was frustrated. Without the support of you, I may not have found myself passionate in LCA and TEA modeling.

In addition, I would like to extend my gratitude to other faculty members serving on my committee: Dr. Raj D. Raman, Dr. Chenxu Yu, Dr. Zhiyou Wen, and Dr. Buddhi Lamsal. Thanks for your valuable suggestions along the way. Your comments and guidance on this project helped me make it more rigorous and precise.

I would further like to thank Dr. David Grewell and other members in the bio-adhesive project. Thanks for their cooperation and academic support when I collected data for the modeling project.

I am also grateful to my fellow Value-Added Bioprocessing (VAB) laboratory members, including (but not limited to) Dr. Ming-Hsun Cheng, Mingjun Ma, and Maria Oliveira. Thanks for their assistance during my time in Iowa State University.

I also want to thank all my sincere friends in Iowa State University, especially Yimeng Li. Thank you for always be there for me and for your unconditional support to help me dealing with all kinds of problems. Also, I want to thank my friends in China who have been in my life for a very long time: Juan Zhang and Mingjie Zhang.

Last but not the least, I would like to thank my family, my parents and all my cousins. Thank you, mom and dad, for giving me the strength to move forward. Without their support, I could not pursue my doctoral degree in Iowa State University. Words could not express my gratitude's to them. Thanks for your endless love!

ABSTRACT

With increasing environmental concerns of fossil fuel, the demand for renewable materials has increased in recent years. One of the most common bio-based feedstock is glycerol, which is mainly generated as a co-product in the biodiesel plant. Glycerol is an extremely versatile compound because of its chemical characteristics, therefore, it is used in synthesizing many molecules, such as polymers and adhesives.

In this project, adhesives were developed from a reversible addition-fragmentation chain-transfer (RAFT) polymerization process; in addition, glycerol was used as the primary feedstock. Due to its novelty, the environmental performance and the economics of adhesive made from the RAFT polymerization process has not been evaluated before. Therefore, the main objective of this dissertation was to explore the environmental impact of this kind of adhesive by life cycle assessment (LCA) method and economic feasibility of this kind of adhesive by techno-economic analysis (TEA). Two kinds of adhesives were produced from the RAFT polymerization process in this dissertation: structural adhesives, and non-structural adhesives. In this study, pressure sensitive adhesive (PSA) was chosen to represent the non-structural adhesive type. Except for these two kinds of adhesives, traditional formaldehyde-based adhesives were also investigated in this project to help us getting an overview of the current adhesive market.

According to the results from life cycle assessment (LCA), we found that for both structural adhesives and non-structural adhesives produced from the RAFT polymerization process, if we adopted biomaterials during the production process, less evidence of greenhouse gas (GHG) emissions were observed in bio-based adhesives than

petro-based ones. When comparing structural adhesives from the RAFT polymerization process with traditional urea formaldehyde adhesives (UF adhesive), which can also be used as structural adhesives, LCA results indicated that even though less global warming air was emitted from UF adhesives, their impacts to human health were much higher than that from structural adhesives produced from the RAFT polymerization process.

The results of techno-economic analysis (TEA) showed that the lowest unit production cost of bio-based structural adhesive was $2.45 /kg and $2.76 /kg for bio-based PSA with the plant scale of 40 t/d. Comparing bio-based structural adhesives with traditional UF adhesives, the unit production cost of structural adhesives from the RAFT polymerization process was higher, but the profit from structural adhesives was higher than traditional UF adhesives.

This dissertation presented the environmental impact and economic feasibility of the novel adhesives from the RAFT polymerization process. The results from this study can provide policy makers and industries with valuable environmental and economic information necessary to produce a more sustainable adhesive.

CHAPTER 1. INTRODUCTION

General Introduction

Adhesives have been discovered in Italy in the Neolithic age (Mazza et al., 2006). At that time, it was a simple birch-bark-tar adhesive used for hafted arrowheads. Ancient Romans, as well as Chinese, made bird lime from the juice of mistletoe as a natural adhesive to catch birds (Donkerwolcke et al., 1998). In 1791, adhesives were used for waterproofing because of their property as natural rubber (Wetzel, 1962), but little improvements were made afterwards. Until the 20th century, formaldehyde-based adhesives have been introduced to produce structural adhesives (Hartshorn, 1986).

As defined in the American Society for Testing and Materials (ASTM) D 907, adhesive is *a substance capable of holding materials together by surface attachment* (ASTM, 2012). There are various theories to explain adhesion phenomenon. Below are four most common theories: mechanical theory, adsorption theory, electrical theory and diffusion theory.

The first theory, as well as the oldest one, is the mechanical theory. Once upon a time, adhesion was considered only happened by flowing and filling pores on the substrates; when it hardened, the substrates were held together mechanically (Petrie, 2007). The mechanical interlocking is a common adhesion type (Bayne et al., 1992); adhesives penetrate cavities in the surface and clings through mechanical forces (Messrs et al., 1964). They are significant on macroscopic scale for fibrous material, such as paper, leather and wood, but not in microscopic scale. Furthermore, the hybrid layer is formed when the monomers permeates the collagen fibril matrix in etched dentin (Marshall et al., 2010).

The second theory is about adsorption. The adsorption theory mainly illustrates the chemical bond and the dispersion force between adhesives and materials. The chemical bonding

could be created through numerous routes, such as covalent, ionic, metallic, and even chelation bonding (Marshall et al., 2010); however, the dispersion force requires two materials are sufficiently close and intimate contact (Allen, 1992). The core of adsorption theory is based on the van der Waals interaction, meaning it should be sufficient for good adhesion if there is a good interfacial contact (Bateup, 1981).

The third one is about the electrostatic attraction between two materials. Even though it is not regarded as one of the major theories, it can be applied appropriately in various scenarios. The electrical double layer at the interface and the surface of the material has been used to explain this theory. These forces are typically dispersion forces and the forces from the interaction of dipoles. This theory proposes that the adhesion phenomenon between adhesives and substrates is caused by the electrostatic charges of opposite sign (Adhesive and glue, 2012).

Last of all, for some specific adhesion phenomenon, diffusion reacts on the interface or segments of polymers, but it is not useful in adhesion between smooth and rigid materials (Allen, 1992). This theory is important only under conditions where macromolecular mobility and mutual solubility are favored to inter-diffusion across the interface (Bateup, 1981). This phenomenon is a two-stage process, and wetting is followed by diffusion. In order to make diffusion occur, adhesives and adherents must be compatible in terms of miscibility, which could be another explanation of why the diffusion theory could only be explained in few scenarios (Petrie, 2007).

There are numerous ways to classify adhesives. Fig. 1.1 shows three common classifications. Adhesive as materials can be broadly classified as natural adhesives and synthetic adhesives by its sources; based on chemical compositions, or polymer compositions, adhesives are divided into thermosetting, thermoplastic, elastomeric, or combinations of these types; due to

different applications, adhesives can be further classified into structural adhesives and non-structural adhesives (Ebnesajjad and Arthur, 2015).

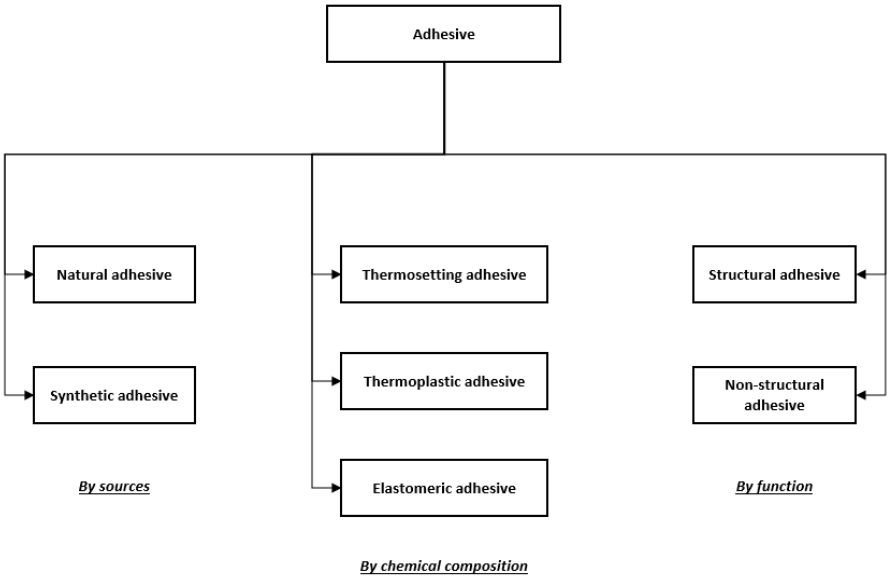

Figure 1.1 A simple classification of adhesives by source, chemical composition and function.

Natural adhesives, including animal-based, vegetable-based adhesives and natural rubber, have been known for a long period. The first commercial natural adhesive plant was founded in 1690 in Holland (Delmonte, 1947). Natural adhesives are inexpensive, easy to apply and have a long shelf life, but they can't provide the structural applications of products. In other words, lack of strength and durability are the disadvantages of natural adhesives (Messmer and Chaudhary, 2015). Thus, there was a decreasing demand of natural adhesives since mid-20th century. However, for non-structural applications, natural adhesives are still widely used, such as labels and book bindings in paper industry (Pike, 2015). Synthetic adhesives are usually applied to all adhesives other than natural adhesives. They could be produced in a constant supply and relatively uniform properties. Moreover, they can be modified in order to meet the best characteristics for the application (Pike, 2015). All structural adhesives are synthetic.

Adhesives can be classified by chemical composition as thermoplastic, thermosetting, and elastomeric. As shown in Fig. 1.2, thermoplastic adhesives don't have cross-linking structure, thus they can be melted reversible without significant change in their properties (Ebnesajjad and Arthur, 2015). The application of thermoplastic adhesives is limited in non-structural applications at low temperatures because of the chemical characteristic. On the contrary, thermosetting adhesives are cure reversible due to their cross-linking structure. They are generally stronger than thermoplastic adhesives and have wider applications in high temperature environment (Messmer and Chaudhary, 2015). Formaldehyde-based adhesives are one of the thermosetting adhesives.

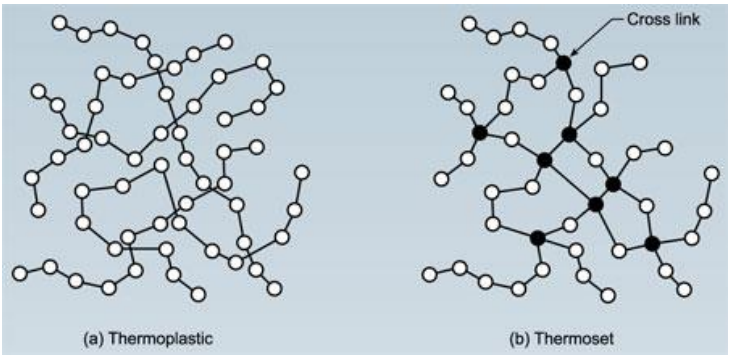

Figure 1.2 Thermoplastic molecules and thermosetting molecules (Recycled Plastic, 2014).

Structural adhesives refer to the adhesives capable of resisting high loads. These include epoxies, cyanoacrylates, and acrylic adhesives. A shear strength larger than 7 MPa is required in a structural bond in order to resist aging (Ebnesajjad and Arthur, 2015). Structural adhesives have been applied successfully in aerospace as well as automotives. On the other hand, non-structural adhesives are typically used as holding adhesives, such as paper binding in office application.

Except for the classification described above, in consumer products, pressure sensitive adhesives (PSA) are perhaps the most common adhesive. PSA is used as non-strucutral adhesive,

such as labels, pressure sensitive tapes, note pads, and automobile trim (Cullen, 1992). The degree of adhesion is influenced by the amount of pressure applied on the surface of the adhesives. The bond is formed when pressure applies to the adherend. PSAs are designed to form a bond at room temperatures; in other words, they may reduce or lose their tack at low temperatures or high temperatures. Therefore, it is important to choose the proper adhesive under various conditions.

There are increasing concerns about the depletion of non-renewable resources and environmental issues in recent dacades (McDevitt and Grigsby, 2014). In order to decrease the public concerns, the use of renewable materials becomes the new trend of adhesives (Rajagopalan et al., 2012). Bio-adhesives could come from many renewable materials, such as enzymes (Kharazipour et al., 1997; Felby et al., 2002), modified vegetable oils (Adekunle, 2007; Dunky et al., 2002), furans (Safe Work Australia, 2009), casein, lignin (Nimtz and Pizzi, 1983), soy proteins, and other proteins (Heimingway and Kreibich, 1984).

Even though the completely cured adhesives could be regarded as non-toxic and safe, the manufacturing process, such as machining and grinding could produce hazardous materials both to human beings and the environment. The environmental impacts of adhesives are not only the issues with human health, but also the issues within nearby community because of the release of volatiles and other wastes. For instance, toluene, one of the solvents, is volatile organic compounds (VOCs) used as carrier fluids in conventional hot-melt adhesives. This solvent is classed as environmental damage and may cause safety issues (De Gray, 1998).

Several factors: toxicity, flammability, hazardous incompatibility, and equipment safety, are considered as the important ones in adhesive bonding procedures (Petrie, 2007). The following Table 1.1 exhibits the legally permissible exposure limit (PEL) for some chemicals

mostly found in epoxy adhesive systems (California Department of Health Service, n.d.). When contacting with the chemicals, the skin, even the eyes, could be affected by the evaporation of chemicals from adhesive systems. The main components of adhesives and sealant materials may be hazardous, even can affect health of human beings. If the adhesive is heated, the vapor and spray mists could irritate the lung; solvents inhaled through the skin may affect the central nervous system in the same way as drinking alcohol. Even though most organic adhesives are not acutely irritating, certain types are capable of causing skin sensitization. Moreover, the curing agents (aliphatic amines, cycloaliphatic amines, and so on) may cause irritation or damage to the skin, eyes, and lungs. Certain types of curing agents may cause damage to organs such as the liver and affect the blood's ability to carry oxygen (Petrie, 2007).

Table 1.1 Legally permissible exposure limits (PEL) in adhesive systems.

Chemical name	**Common Abbreviation**	**California OSHA PEL (ppm)**
n-Butyl glycidyl ether	BGE	25
Isopropyl glycidyl ether	IGE	50
Phenyl glycidyl ether	PGE	1
Diethylenediamine	DETA	1
Toluene	N/D	100
Xylene	N/D	100
Methyl ethyl ketone	MEK	200

Since VOC emissions from urea formaldehyde (UF) adhesives also became an environmental concern in recent decades, researchers began to focus on the replacement of the formaldehyde-based adhesive systems (Wiglusz et al., 2002). In 2009, Kim conducted an experiment to add polyvinyl alcohol (PVA) to natural tannin adhesives. As a result, a better bonding effect and a high level of wood penetration was observed compared with commercial

adhesives. The emissions from formaldehyde was lower by adding PVAs, and they could be further reduced when UV curable urethane acrylate was coated (Kim, 2009). However, the excellent bonding properties and relatively cheap price of formaldehyde-based adhesives made them rather competitive in the current market.

In order to reduce the environmental burden from petroleum-based adhesives, researchers in Iowa State University developed a novel bio-adhesive process from the reversible addition-fragmentation chain-transfer (RAFT) polymerization process. RAFT polymerization process is first reported in late 1990s, and soon it becomes one of the most popular polymerization techniques because of its versatile synthetic characteristics (Semsarilar and Perrier, 2010).

RAFT polymerization process is exhibited in Fig. 1.3. As indicated by Hao et al., it starts with an initiation step to create a radical; after that, the radical is reversibly added to a chain transfer agent (CTA) to generate a re-initiating group ($R\cdot$). Then, $R\cdot$ can re-initate the polymerization process; and the polymer chain keeps growing followed by the re-initation process until a termination reaction happens.

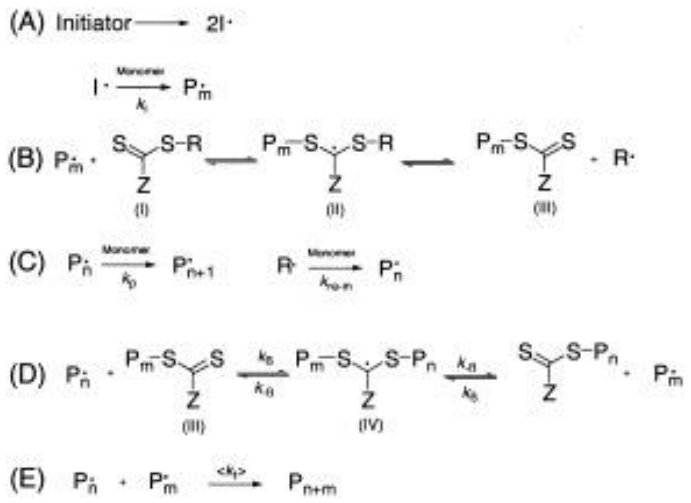

Figure 1.3 Generally accepted mechanism of the RAFT polymerization process (Hao et al., 2003)

RAFT is regarded as a green and sustainable process because it has minimum environmental impacts in chemical products and processes (Semsarilar and Perrier, 2010). However, RAFT has not yet been applied in bio-adhesive production.

Life Cycle Assessment

Life cycle assessment (LCA) is an analytical methodology used to quantify the environmental impact of a given product throughout its life cycle. LCA has been employed to evaluate environmental issues since 1970s (Guinée et al., 2011). Earlier LCA studies were performed using different approaches and terminologies, but without a common theoretical framework, the results differed greatly even when the objects were the same (Guinée et al., 1993). In the 1990s, the International Standard Organization (ISO) established the first international standard of LCA: *ISO 14040: 'Environmental management' – life cycle assessment – Principles and framework'* (ISO, 1997). Several years later, in 2006, ISO published the second international standard of LCA: *ISO 14044: 'Environmental management' – life cycle assessment – Requirements and guidelines'* (ISO, 2006). These standards provided a standardized framework and terminology for LCA practitioners. As suggested by ISO, LCA can be used to identify hotspots to improve products from environmental perspective, to assist in making decision such as strategic planning and environmental product declaration (ISO, 1997). Gradually, LCA becomes a critical methodology encouraged by governments worldwide in environmental policies and activities.

Typically, LCA investigates the environmental impact of a product over its entire life cycle, from raw materials production, main products production, utilization to end-of-life treatments. It consists four components as shown in Fig. 1.4: (1) goal and scope definition, (2) inventory analysis, (3) impact assessment, and (4) interpretation (ISO, 1997).

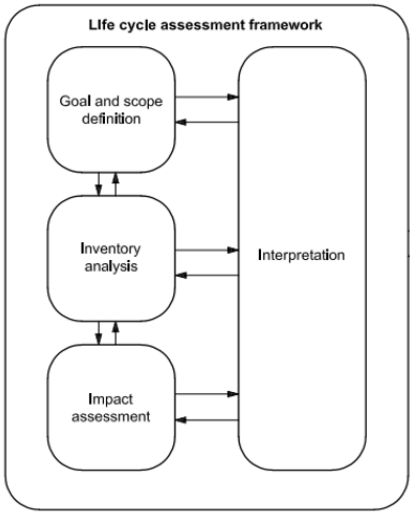

Figure 1.4 Components of process-based LCA (ISO, 1997).

The first step is goal and scope definition. The objectives or purposes of the study are declared in this step. System boundary, which defines processes that will be included, or excluded from the system, is described. Functional unit (FU) is also chosen in here. FU must be consistent and equivalent throughout the study in order to directly compare different systems (Borrion et al., 2012). In addition, description of all assumptions of the LCA study, allocation method and system expansion, and data requirements are also specified in this goal and scope definition step.

The second step is inventory analysis. Typically, inventory analysis is the most time consuming step during the LCA study. In this step, data is collected and calculated based on the material inputs and environmental outputs of a given product. More specifically, the materials and energy used throughout the product's life cycle, and the resulting wastes or emissions from the product's activities are quantified in this process.

After inventory analysis, the third step is impact assessment. This step is used to evaluate the potential environmental impacts according to inventory analysis. Based on the likely long

term damage to the environment, such as climate change, acidification and eutrophication, the life cycle inventory data is classified and characterized into a wide variety of impact categories. Impact categories can be chosen from inventory-level: mid-point indicator and end-point indicator (Sandin et al., 2016). Mid-point indicator, also known as problem-oriented approach, reflects the cause-effect chain from activities (Ortiz et al., 2009); while end-point indicator, also known as damage-oriented approach, is often expressed in three areas: human health impacts, ecosystem quality impacts, and resource depletion impacts (Geodkoop et al., 2013). The selection of impact assessment method is mainly depend on the goal of the LCA study.

The interpretation step is an iterative step that can be taken place within the interpretation itself and with other steps of the LCA study. By taking into account of the goal and scope, this step could be used to evaluate the inventory data and impact assessment results and to make recommendations on reduction of negative impacts. In addition, it can check the consistency of the results with the objectives of the LCA study. In order to identify the significant issues, sensitivity analysis and uncertainty analysis, both are used to test the uncertainties associated with LCA methodology, are often recommended (Messmer and Chaudhary, 2015).

Except for the above described process-based procedures suggested by ISO, other LCA methodology approaches have been developing in recent years. Economic input-output LCA (EIO-LCA) is one of the emerging LCA methods. It utilizes economic input-output data to quantify the environmental and energy for each sector. It is more complete in the system-level and less time consuming as compared with process-based LCA (Suh and Huppes, 2003). However, EIO-LCA doesn't include the use phase or the end-of-life treatment phase; it only considers carbon footprint of the supply chain. Another LCA method named hybrid LCA, which combines process-based LCA and EIO-LCA, has been developed in order to maintain the

positive aspects of these two approaches. Furthermore, life cycle sustainability assessment (LCSA) and social life cycle assessment (sLCA) have also been introduced as new trends in LCA domain (UNEP/SETAC, 2011). To date, LCA has been widely applied in biofuel production and pharmaceutical drug production (Raymond et al., 2010; Clarens et al., 2010). As for adhesive production, little LCA literatures are available.

LCA has been conducted to investigate the environmental impacts of several wood adhesives used in wood construction. Messmer and Chaudharay conducted a cradle-to-gate LCA study of four different wood adhesives in 2015 (Messmer and Chaudhary, 2015). In that study, a functional unit of 1 kg of adhesive with solids content of 100% was chosen; polyurethane (PUR) adhesive, melamine urea formaldehyde (MUF) adhesive, phenol formaldehyde (PF) adhesive, and phenol resorcinol formaldehyde (PRF) adhesive production were investigated. The results showed that PUR has the lowest environmental impacts for the production of timber according to the endpoint impact assessment method (ReCiPe method). In terms of the contribution analysis, the production of raw material has the highest impact score for all four types of adhesives.

Life cycle inventory (LCI) analysis of formaldehyde-based adhesives has also been developed by Dr. Wilson in 2009 (Wilson, 2009). He selected urea formaldehyde (UF) adhesive, melamine urea formaldehyde (MUF) adhesive, phenol formaldehyde (PF) adhesives, and phenol resorcinol formaldehyde (PRF) adhesive produced in 2005 as target products. The LCI results showed that by producing 1kg of liquid formaldehyde-based adhesive, MUF adhesive has the highest carbon footprint (1.775 kg CO_2-eq/kg of resin), followed by UF adhesive (1.608 kg CO_2-eq/kg of resin) and PRF (1.394 kg CO_2-eq/kg of resin). Even though PF adhesive has the lowest carbon footprint (1.322 kg CO_2-eq/kg of resin) in liquid form (47% of solids), it has the highest carbon footprint (2.788 kg CO_2-eq/kg of resin) when producing as 100% solids.

In 2014, McDevitt and Grigsby compared the environment impacts of bio-chemical and petro- chemical adhesives used in fiberboard production. By using *Eco-Indicator* 99 (EI 99) impact method, the authors found that for the entire life cycle, the petro-chemical adhesives have a 22% higher environment impact than the bio-chemical adhesives (McDevitt and Grigsby, 2014). Other comparisons between petro-chemical and bio-chemical adhesives were exhibited in Table 1.2, along with the Fig. 1.5.

Table 1.2 Comparison of petro- and bio- chemical adhesives (McDevitt and Grigsby, 2014).

	Comparisons based on EI 99
Functional unit (FU)	1m^2 of medium-density fiberboard
Fossil fuel changes	39% lower of bio-adhesives
Climate changes	9% lower of bio-adhesives
Resource depletion	40% larger for the petro-based adhesives
Ecosystem quality	59% more in the bio-adhesives

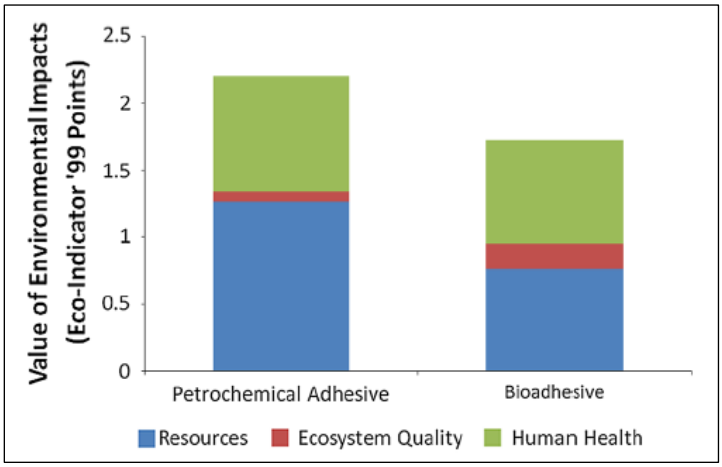

Figure 1.5 Life cycle environmental impacts comparison between petro-chemical adhesive and bio-chemical adhesive (McDevitt and Grigsby, 2014).

Because of increasing restrictions on the release of VOCs to the atmosphere, there are less trends from using organic solvents and dispersing media in adhesive systems. As indicated by Pichelin et al. (1999), any species with a strong negative charge under alkaline condition was capable to render bonded panels of extremely low formaldehyde emission; in other words, the adhesives based on hexamine could reduce the environment impact from formaldehyde. The results from Pichelin et al. showed that tannin-hexamine adhesive was a very environmentally-friendly product.

Mati-Baouche et al. explored the application of chitosan as an adhesive in 2014 (Mati-Baouche et al., 2014). Chitosan is a well-known polysaccharide typically used in biomedical and bio-adhesive field. One of the advantages of using chitosan as bio-adhesive was due to its relatively low environmental impacts as compared with chemical adhesives as suggested by the authors. But there are no data available in LCA literatures about chitosan adhesives.

Techno-Economic Analysis

Techno-economic analysis (TEA) is the study that combines the technical aspects of a project with its economic aspects. It can be used to evaluate the economic feasibility of a specific project, investigate the cash flow over the project's life time, and to compare different technologies from economic perspective (Lauer, n.d). Generally speaking, TEA includes two steps. First, researchers need to develop the theoretical configuration and perform the mass and energy balance; then, cost estimation is conducted based on step one (Swanson et al., 2010).

Three major components are included in a typical TEA study: total capital investment (C_{TCI}), annual operating cost (C_{AOC}), and revenues. Table 1.3 and Table 1.4 exhibits the main items included in C_{TCI} and C_{AOC}.

Total capital investment (C_{TCI}) can be broken down into three parts: direct fixed cost (C_{DFC}), working capital (C_W), and start-up and validation costs (C_S). Direct fixed cost is the cost involved in installation of the facility. All items listed in C_{DFC} are quantified based on the equipment purchase cost (C_P). Indirect costs, which are not directly involved during facility installation, refer to engineering cost and construction cost. As for other cost, it contains contractor's fee and contingency cost. Indirect cost and other cost are calculated based on the direct fixed cost. In terms of working capital and start-up and validation cost, they are usually assumed to be 10% and 15% of the C_{DFC} (Peter et al., 2015).

Table 1.3 Typical items listed in total capital investment (C_{TCI}).

Total capital investment (C_{TCI})
1. Direct fixed capital cost (C_{DFC})
1) Direct cost (C_{DC})
Equipment purchase cost (C_{PC})
Piping
Instrumentation
Insulation
Electrical facilities
Building
Yard improvement
Auxiliary facilities
Installation
Land

Table 1.3. (continued)

Total capital investment (C_{TCI})
2) Indirect cost (C_{IC})
Engineering
Construction
3) Other cost (C_{OC})
Contractor's fee
Contingency
2. Working capital (C_W)
3. Start-up and validation cost (C_S)

Annual operating cost (C_{AOC}) contains four parts: materials cost (C_M), utility cost (C_U), labor cost (C_L) and facilities cost (C_F). Annual operating cost changes based on market fluctuation and economic conditions. In utility cost category, annual cost of electricity, water and steam associated with the production process is quantified. As for facilities cost, it includes maintenance cost, depreciation, insurance, tax and plant overhead fee.

Table 1.4 Typical items listed in annual operating cost (C_{AOC}).

Annual operating cost (C_{AOC})
1. Materials cost (C_M)
2. Utilities cost (C_U)
3. Labor cost (C_L)
4. Facility cost (C_F)

Revenue from TEA is calculated from the product's annual amount and its current market selling price. Furthermore, gross profit and other profitability evaluation criteria, such as return on investment and payback period, can be evaluated based on capital investment, annual operating cost, and revenues (Table 1.5).

Table 1.5 Typical items calculated in profit analysis.

Profit analysis
$Revenues\ (\$) = Selling\ price(\$/kg) \times Annual\ amount(kg)$
$Gross\ profit\ (\$) = Revenues(\$) - (C_{AOC} - C_F)(\$)$
$Return\ on\ investment\ (\%) = \frac{Net\ profit}{Total\ investment} \times 100$
$Payback\ times\ (years) = \frac{1}{Return\ on\ investment}$
$Unit\ production\ cost\ (\$/kg) = \frac{Total\ investment\ (\$)}{Unit\ reference\ flow\ (kg/y)}$
$Net\ present\ value\ (\$) = \sum_1^n \frac{Net\ cash\ flow}{(1+i)^n}$

TEA has been extensively explored in the field of renewable energy. However, as for adhesive production systems, TEA has not been applied for techno-economic evaluation purpose.

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CHAPTER 2. OBJECTIVES AND DISSERTATION ORGANIZATION

The target product in this dissertation is the bio-adhesive made by the RAFT polymerization process. The overall objective is to evaluate the environmental impacts of this bio-adhesive by using life cycle assessment (LCA) approach and to explore the economic feasibility by using techno-economic analysis (TEA) methodology of the following adhesives: structural bio-adhesive and non-structural bio-adhesive, in particular, pressure sensitive bio-adhesive. In addition, traditional formaldehyde-based adhesive has also been investigated by LCA and TEA method in order to gain better understanding of adhesive production systems.

Specifically, the sub-objectives of this dissertation are listed as below:

1. To quantify the environmental impacts (cradle to gate) and the economic feasibility of structural bio-adhesive from the RAFT production process.
2. To quantify the environmental impacts (cradle to gate) and the economic feasibility of non-structural bio-adhesive (PSA) from the RAFT production process.
3. To explore the environmental impacts (cradle to gate) and the economic feasibility of traditional formaldehyde-based adhesive.

Chapters in this dissertation are organized based on the above objectives. Chapter 1 introduces fundamental concepts and approaches on LCA and TEA. Chapter 2 demonstrates the overall objectives of this dissertation. Chapter 3 and Chapter 4 focus on structural bio-adhesive from LCA and TEA aspects (Objective 1). Chapter 5 and Chapter 6 evaluate the environmental impact and cost of PSA (Objective 2). Chapter 7 and Chapter 8 investigate the impacts on formaldehyde-based adhesives (Objective 3 and 4). Chapter 9 provides implications from this project. Chapter 10 offers recommendations for future studies.

CHAPTER 3. CRADLE TO GATE LIFE CYCLE ASSESSMENT OF THE STRUCTURAL BIO-ADHESIVES DERIVED FROM GLYCEROL

A paper submitted to *Food and Bioproducts Processing.*

Abstract

Because of increasing environmental concerns about petroleum-based adhesives, the replacement of petro-based adhesives has attracted much attention. The purpose of this paper was to evaluate the potential environmental impact of glycerol-based structural bio-adhesive production accomplished through the reversible addition-fragmentation chain transfer (RAFT) process. In this study, two pathways of glycerol production were considered: bio-based and petroleum-based production processes. GaBi 6 software was employed to perform this cradle to gate life cycle assessment (LCA) study. Several key parameters for life cycle analysis were analyzed, including: energy requirements, global warming potential (GWP), acidification potential (AP), eutrophication potential (EP), and human health effects (cancer and non-cancer). Various allocation methods (energy allocation, physical allocation, and economic allocation method) were also explored in this study. Our results showed that bio-glycerol based structural adhesive has a lower environmental impact in general compared to petro-glycerol based structural adhesive. Higher environmental impacts throughout the structural bio-adhesive life cycle were observed by adopting energy allocation method. The key factors that influence the global warming potential are determined to be electricity source, followed by production yield. This LCA study is able to provide useful information for developing sustainable biomaterials and processes. Underlying issues associated with the process were also discussed in this study.

Keywords

Life cycle assessment (LCA); Glycerol; Structural bio-adhesive; RAFT polymerization; Allocation method; Sensitivity analysis.

Introduction

In recent decades, increasing environmental concerns and resource depletion of petroleum-based materials have led to exploring their replacement, and the expansion in the use of bio-based material is expected to play a crucial role in the chemical and fuel industries (Lichtenthaler, 2010). As projected by the U.S. Energy Information Administration (U.S. EIA), in 2016, the total petroleum and other liquids consumption is 18.28 quads (1.83E+16 BTU) worldwide (U.S. EIA, 2017). Chemicals have a strong dependence on petroleum refineries because they produce the majority of chemicals; nearly 4% of the world's oil is used for chemical and plastic production (Nossin PMM, 2009).

Adhesive has been widely applied in many areas, for example, wood production, paper bonding and packaging, automotive, and aerospace. Taking the wood adhesive market as an example, by 2025, the wood adhesive market size will be $6.18 billion, as forecast by *Grand View Research* (Grand View Research, 2017); based on the *Markets and Markets* report, the adhesive market is expected to increase to $63.50 billion by 2021 (Markets and Markets, 2017).

Bio-adhesives are natural polymers, usually derived from biological materials, such as proteins and lignin. They are renewable, widely distributed, recyclable and readily available in many forms. While protein has been used as the primary choice in formulating wood adhesive for centuries (Frihart, 2016), the formulations of protein-based wood adhesive is sensitive to some specific sources and sometimes become time-consuming in terms of bonding processes. In

recent years, the main research on protein-based adhesives has been focused on vegetable proteins such as those in soybeans due to their abundance and relatively low cost (Frihart and Birkeland, 2016). As for the lignin, it is the second most abundant renewable source in nature with a quite complex structure. Even though it is a promising raw material, the high cost for purer lignin and its limited number of reactive sites are major problems related to lignin-based wood adhesive production (Frihart, 2016).

Glycerol, discovered in 1783 by a Swedish chemist, and also known as 1, 2, 3-propanetriol, has been a well-known chemical for centuries. The production of glycerol increased rapidly at the end of the nineteenth century due to processing of natural fats and oils (Behr et al., 2008). Nowadays, glycerol is mainly generated as a co-product of fatty acid methyl esters (FAME), also known as biodiesel. The chemical reaction that takes place during biodiesel production is shown in Fig. 3.1.

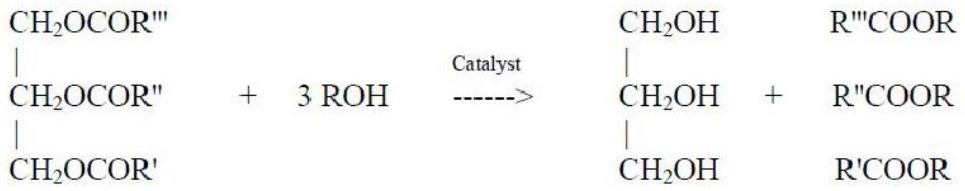

Figure 3.1 Chemical reaction of biodiesel.

The biodiesel market reached 1,568 million gallons in 2016 according to the U.S. EIA, and compared to 2015, it increased by nearly 20% (1,268 million gallons) (U.S. EIA, 2017). A great number of glycerol has been produced as a by-product of the biodiesel plants. The global glycerol market was valued at $2.19 billion in 2015 based on the *Markets and Markets* report, and it is expected to achieve $3.12 billion by 2021 (Markets and Markets, 2017). The wide application of glycerol has mainly occurred because of its chemical characteristics and

availability on the market. Glycerol is an extremely versatile compound, which is great for the synthesis of many organic chemicals, such as ethers, esters, carboxylic acids, and polymers (Tao et al., 2013).

This study uses the reversible addition-fragmentation chain transfer (RAFT) polymerization process to produce a high molecular weight polymer and structural bio-adhesive as the final product. The RAFT polymerization process, one of the living radical polymerization (LRP) technique, was first reported in the late 1990s. It is also a free-radical polymerization process. The best-known characteristic of the LRP technique is that it can continue the polymerization process even when the initial feed is exhausted (Semsarilar and Perrier, 2010). Over the past decades, the RAFT polymerization process becomes one of the most popular technique due to its versatile synthetic characteristics. For instance, this process can be applied to most vinyl monomers, and it can be compatible with a variety of conditions (Zhang et al., 2015). Moreover, it has been proven as a useful technique for synthesizing hydrophilic polymers (Lowe and McCormick, 2007).

In general, the RAFT polymerization process starts with an initiation step aiming at creating a radical (Fig. 3.2 (A)), and the radical ($P_m^{\cdot}$) reversibly added to the chain transfer agent (CTA) to create a re-initiating group ($R^{\cdot}$) (Fig. 3.2 (B)). Chain transfer agent (CTA), also called the RAFT agent, is a critical component in the RAFT polymerization process, the key to a successful polymerization process. Afterwards, the $R^{\cdot}$ re-initiates the polymerization process to produce another radical ($P_n^{\cdot}$) (Fig. 3.2 (C)). Following re-initiation, the main equilibrium RAFT polymerization process dominates growing the polymer chain (Fig. 3.2 (D)) until a termination reaction occurs (Fig. 3.2 (E)) (Semsarilar and Perrier, 2010).

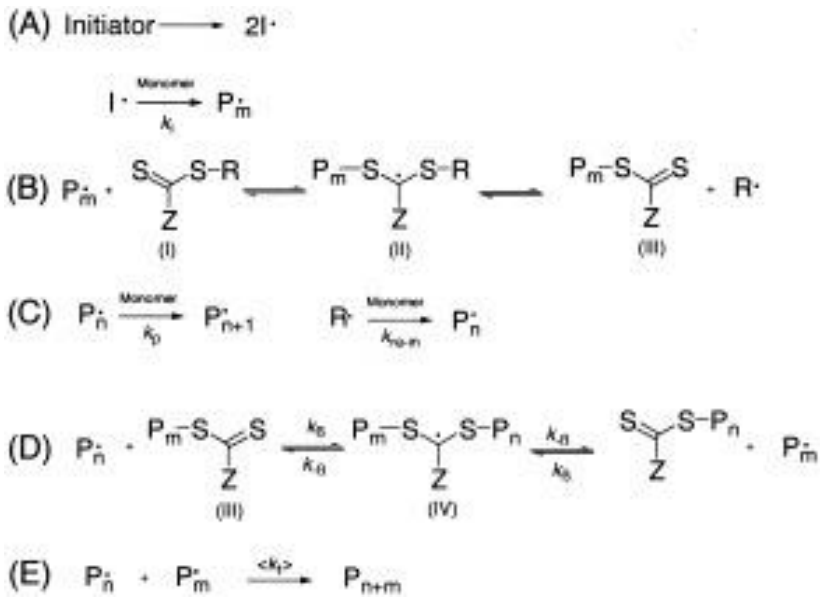

Figure 3.2 Generally accepted mechanism of the RAFT polymerization process (Hao et al., 2003).

The RAFT polymerization process can be carried out under environmental-friendly conditions, such as with water-based solvent (Lowe and McCormick, 2007) or ionic liquids (Shakraborty et al., 2014). Moreover, the RAFT polymerization process can be applied to renewable resources such as organic and inorganic renewable materials that can be polymerized via RAFT polymerization (Boyer et al., 2009). However, supplied of a number of renewables being used to manufacturing products are low in the present; mostly because economic value is the driving factor of the industry, and renewables do not have economic parity with petroleum goods (Hernandez et al., 2014).

In 2013, Cochran et al. broadened the RAFT polymerization application for making novel thermoplastic homopolymer and block copolymers, which are derived from the plant oil or animal oil (U. S. Patent US 2014/0343192 A1, 2014). Recently, researchers in Iowa State University developed a novel structural bio-adhesive production process based on the RAFT polymerization process. Though the RAFT polymerization process is regarded as a green and

sustainable process in chemical products (Semsarilar and Perrier, 2010), no study investigated the environmental impact of the bio-adhesive production system as to the authors' knowledge.

In this work, the potential environmental impact of the bio-adhesive production process was evaluated from the life cycle perspective. Life cycle assessment (LCA) has been developed in 1970s. Earlier LCA work mainly focused on standardization activities, such as establishing the framework, terminology, and platform for LCA methods. The two currently used international standards, ISO 14040: 'Environmental management – life cycle assessment – principles and framework' and ISO 14044: 'Environmental management – life cycle assessment – requirements and guidelines', were developed in 2006 by the International Standard Organization (ISO, 2006). Afterwards, LCA has subsequently boomed in many areas, including the European Union, the United States, Japan, Korea and China (Guinée et al., 2011). Governments worldwide encourage the application of LCA due to its advantages in strategic planning and identifying the opportunities to improve the environment in their life cycle (ISO, 1997).

According to ISO 14044, four steps are included in an LCA study (Fig. 3.3). The first phase is the description of goal and scope, in which the objectives of the study, the functional unit used in this study, the system boundaries and associated assumptions are made. The second phase is the life cycle inventory (LCI) analysis, which includes compilation of the inputs and outputs for each process throughout the entire life cycle. The third phase is the life cycle impact assessment. In this step, emissions are categorized based on the impact categories and then it is converted to impact units to make the environmental impact comparison. The fourth phase is the interpretation. It is an iterative step used to interpret the results from the inventory analysis and the impact assessment.

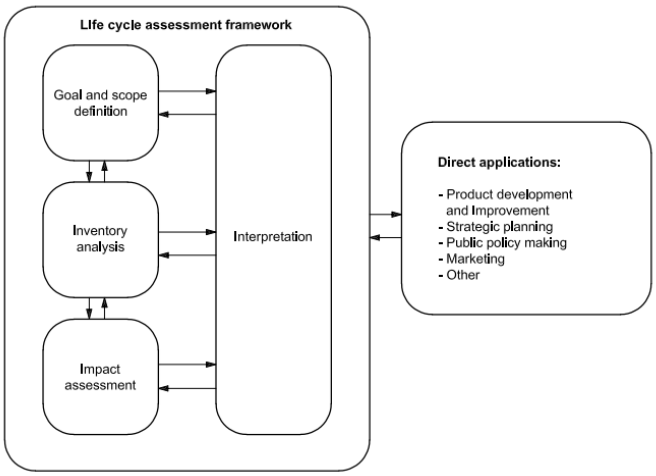

Figure 3.3 Stages of an LCA study (International Standard Organization, 1997).

In 2014, McDevitt and Grigsby compared the environment impact of bio- and petro-chemical adhesives used in fiberboard production in New Zealand. By using Ecoindicator 99 impact method, the authors found that for the entire life cycle, petro-chemical adhesives have nearly 22% higher environment impact than bio-chemical adhesives. As for ecosystem quality, biobased adhesive decreased by around 39% than petro-chemical adhesives (McDevitt and Grigsby, 2014). However, due to the geographic limitation in their study, the environmental impact result may vary from place to place.

The main objective of our study is to evaluate the environmental impact associated with the structural bio-adhesive production process using the RAFT polymerization technique. As mentioned in previous, even though glycerol is mainly produced from biodiesel plants, it can also be produced from oil refinery plants. These two scenarios are all adopted in this study in order to fully understand the environmental impact from the production process. The functional unit selected for this study was the production of 1 kg of the final product.

Methods

In this study, life cycle assessment (LCA) method was used to evaluate the environmental impact from structural bio-adhesive production process. LCA was performed according to the International Standard Organization – ISO 14044:2006 environmental management --- life cycle assessment--- requirements and guidelines (ISO, 2006). It is assumed that the chemical plant is located in central Iowa. GaBi 6 software, purchased from PE international, was adopted to performing the LCA analysis. The description of the systems, life cycle inventory analysis, and life cycle impact assessment are given in this section.

Description of systems

Two scenarios of the structural adhesive production process were modeled with respect to their environmental impact. Scenario 1 is the production of structural adhesive derived from bio-glycerol and Scenario 2 is the production of structural adhesive derived from petro-glycerol, with the origin of the glycerol being the obvious largest difference between these two scenarios. In Scenario 1 (Fig. 3.4), glycerol comes from the biodiesel industry; while in Scenario 2 (Fig. 3.5), glycerol comes from the petroleum refinery plant.

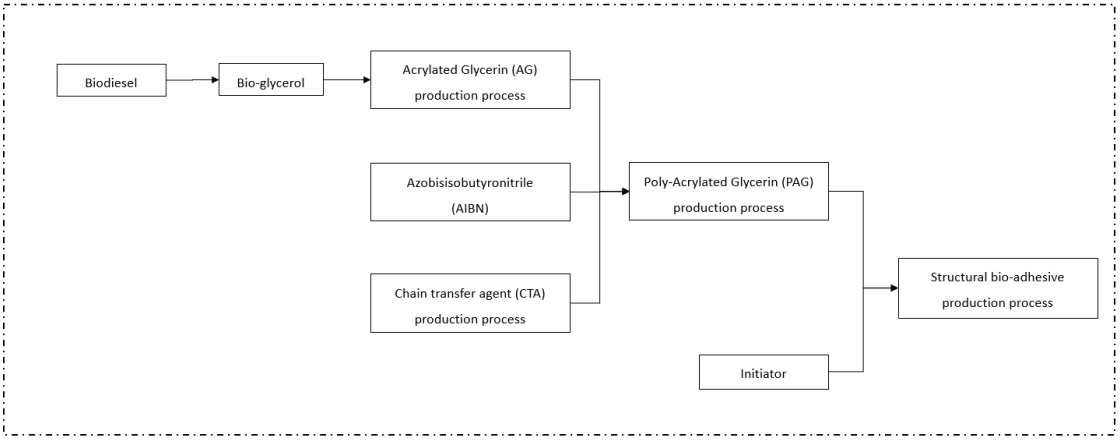

Figure 3.4 Simplified flowchart of the overall structural bio-adhesive production process (Scenario 1).

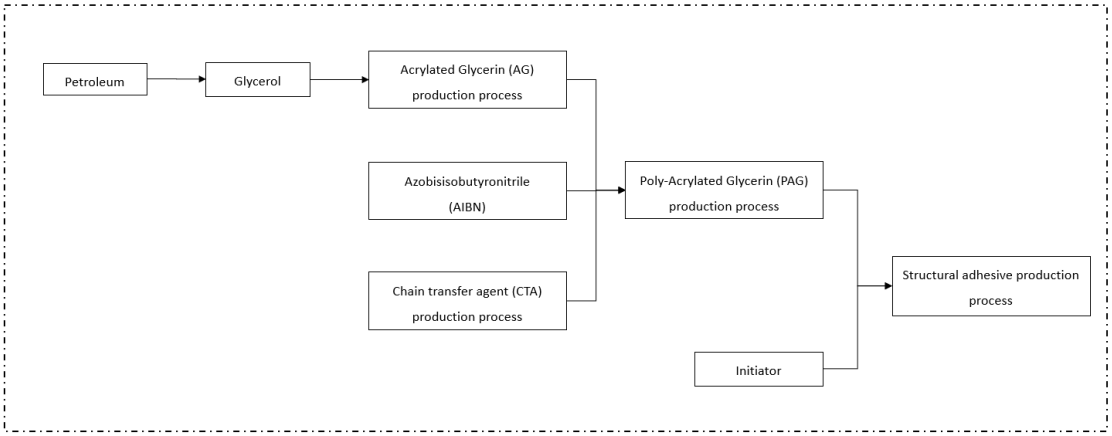

Figure 3.5 Simplified flowchart of the overall structural adhesive production process (Scenario 2).

This study is a cradle-to-gate life cycle assessment; in other words, the system boundary begins with the extraction of raw materials, and ends when the structural adhesive is produced. The overall structural adhesive production process is divided into four parts: a) an acrylated glycerol (AG) production process (Fig. 3.6); b) a chain transfer agent (CTA) production process (Fig. 3.7); c) a poly-acrylated glycerol (PAG) production process (Fig. 3.8); and d) a structural adhesive production process (Fig. 3.9).

The glycerol in Scenario 1 originates from a biodiesel plant, and its data was collected from a U.S. Department of Energy's report (Sheehan et al., 1998). The biodiesel production process starts with soybean grains cultivation, then soybean is crushed to produce the soybean oil, after which the soybean oil is converted into biodiesel through a transesterification process that produces crude glycerol (80% wt.) as a co-product. It is assumed that 97% of the production yield is obtained of this biodiesel production plant. As suggested by the Sheenhan et al., approximately 150 kg of crude glycerol is generated during production of 1,000 kg of biodiesel. The process requires 1,037 kg of soybean oil, 90 kg of methanol, 356 kg of water and catalysts such as sodium hydroxide, as raw inputs when producing 1,000 kg of biodiesel. The energy input

includes 28.9 kWh of electricity and 1,356 Mt of steam required to produce 1,000 kg of biodiesel (Sheehan et al., 1998). In Scenario 2, glycerol is obtained from petroleum refinery. It was developed in 1959 for the industrial synthesis (Cespi et al., 2014). This is mainly an oxidation process in the fixed-bed reactor. Propylene is oxidized under the temperature of 300-320°C, and the pressure required for this process is around 150-250 kPa. The yield is assumed to be 75% based on literatures.

In addition, the physical allocation factor (mass ratio) between glycerol and biodiesel is calculated to be 1 over 6.7. While Sheehan et al. suggested using mass allocation because it introduced fewer practical problems during the interpretation phase (Sheehan et al., 1998), other allocation methods (economic factor and energy factor) have been employed in other reports and literatures (Elsayed et al., 2003; Hill et al., 2006). In our study, we will explore the environmental impact resulting from these three allocation methods. The economic allocation factor between glycerol and biodiesel is assumed to be 1 over 51. As for the energy values, LHVs (lower heating values) have been used for comparison. The energy allocation factor between glycerol and biodiesel is assumed 1 over 1.33. Table 3.1 below gives a summary of the allocation factors.

Table 3.1 Assumptions of the allocation factors used in structural bio-adhesive production.

	Mass value	**Economic value**	**Energy value**
Biodiesel	1 kg (Sheehan et al., 1998)	3.22 $/gal (DOE, 2017)	117,093 BTU/gal (Iowa State University, 2017)
Glycerol	0.15 kg (Sheehan et al., 1998)	46-48 ¢/lbs. (ICIS, 2017)	25.30 MJ/kg (University of Strathclyde, 2017)

Scenario 2 shown in Fig. 3.6 describes the acrylated glycerol production process used in the petroleum refinery plant, with a model of glycerol production process built on the GaBi database. For both scenarios, as soon as glycerol is obtained, acrylic acid with catalysts (Phenothiazine and Amberlyst-15) are added to produce acrylated glycerol (AG). The AG production process takes place at 100°C and lasts for about 5 hours.

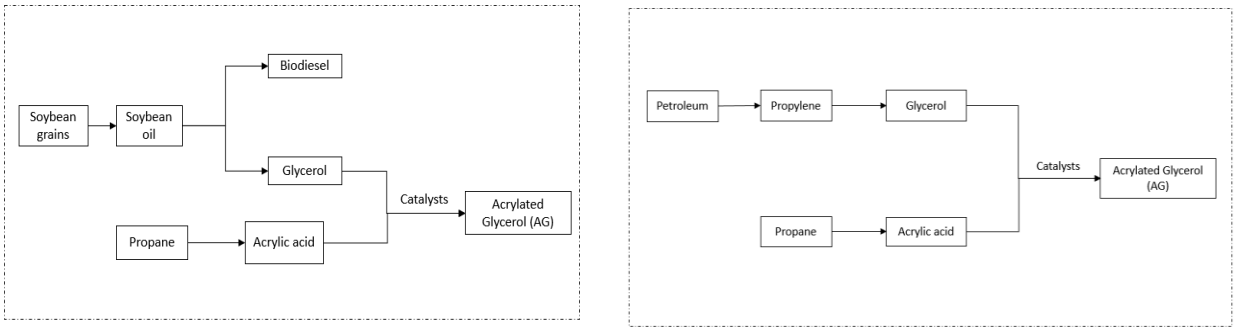

Figure 3.6 Acrylated glycerol (AG) production process (Scenario 1: left; Scenario 2: right).

Afterwards, the RAFT polymerization is conducted as a two-step process, with the initial step used to produce the chain transfer agent (CTA). Ethanethiol is first neutralized with potassium hydroxide for about 30 minutes, then carbon disulfide reacts with the pH neutral solution for about 30 minutes, after which 3-chloro-2-butanone is added to produce the CTA. The whole CTA production process happens in an acetone solution, and the acetone recycle rate suggested by polymerization professionals is assumed to be 97%. Mild temperature and pressure are used during the CTA production process.

The second step of the RAFT polymerization is reaction between AG and CTA, with Azobisisobutyronitrile (AIBN) used as the catalyst in the poly-acrylated glycerol (PAG) production process. This reaction proceeds at 70°C for approximately 4 hours.

After the RAFT polymerization process, water is added to precipitate the polymer, followed by initiator (4, 4'-azobis) used to produce the structural bio-adhesive. The final product is preserved in liquid form.

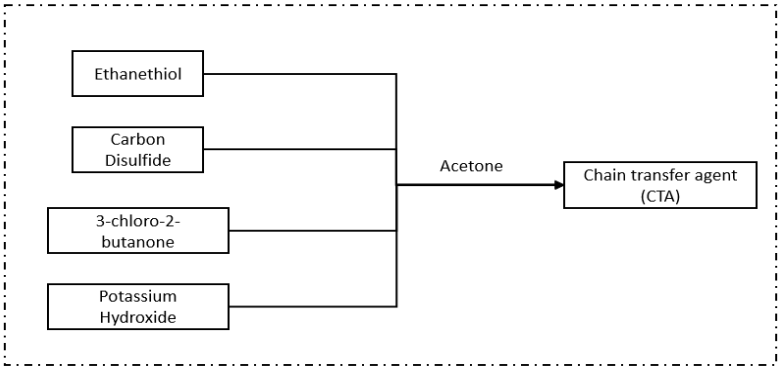

Figure 3.7 Chain transfer agent (CTA) production process.

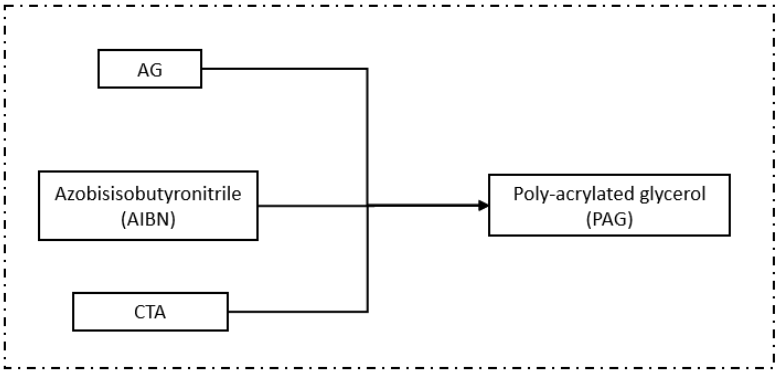

Figure 3.8 Poly-acrylated glycerol (PAG) production process.

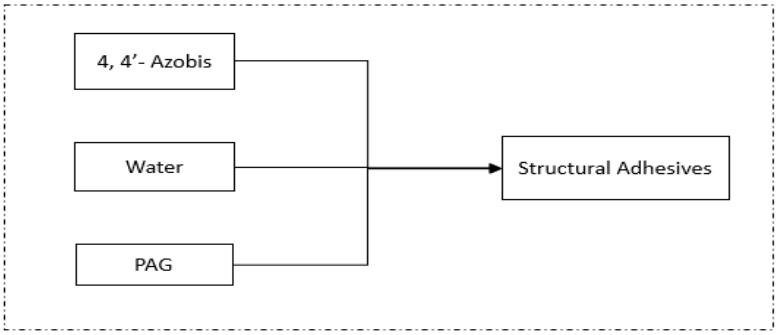

Figure 3.9 Structural adhesive production process.

Life cycle inventory analysis

In this study, the data was mainly collected from Iowa State University's research laboratory results. Literature, including reports and patents, was also used as a source of background data. Databases such as EcoInvent, GaBi, and U.S. life cycle inventory (U.S. LCI), were employed to cover data gaps.

The electricity production data was obtained from the U.S. Energy Information Administration (U.S. EIA) (EIA, 2016). In Iowa, nearly 60% of electrical power is generated through fossil fuels, while about 35% comes from the renewable sources. The electrical data was used in calculation of life cycle impact assessment, while data for energy consumption happening during chemical production processes is collected using the SuperPro Designer v9.5 software.

Table 3.2 Main mass balance of the structural bio-adhesive production process.

	Materials	**Input (kg)**	**Output (kg)**
AG process	Glycerol	0.63	
	Acrylic acid	0.49	
	AG		1
	Water		0.123
CTA process	Ethanethiol	0.13	
	Carbon disulfide	0.31	
	3-Chloro-2-butanone	0.43	
	Potassium hydroxide	0.13	
	OXCART		1
	KCl		0.286

Table 3.2. (continued)

	Materials	Input (kg)	Output (kg)
PAG process	AG	1	
	OXCART	1.45E-04	
	AIBN	2.46E-05	
	PAG		1

The mass balance for each process is summarized in Table 3.2. The transport distance of materials within the state of Iowa is assumed to be 50 miles. Truck, powered by diesel, was chosen as the transportation vehicle. Its tailpipe emissions were assumed to correspond to a 'Euro 5' vehicle.

Life cycle impact assessment

Two impact assessment methods, TRACI 2.1 and Eco-Indicator 99, were chosen in this study. In 2003, the U.S. Environmental Protection Agency (U.S. EPA) developed TRACI, short for *Tool for Reduction and Assessment of Chemicals and Other Environmental Impacts* (Bare et al., 2003). TRACI is a mid-point impact assessment approach, also known as problem-oriented approach (Ortiz et al., 2009). The TRACI impact method reflects the cause-effect chain, with impact categories that include ozone depletion, climate change, acidification, eutrophication, smog formation, human health impacts, and ecotoxicity (EPA, 2016). Eco-Indicator 99 (EI 99) is an end-point assessment approach, also known as damage-oriented approach. EI 99 considers three types of environmental damage (Table 3.3): human health, ecosystem quality and resources. The outcome of EI 99 is expressed in one single score for total environmental impact (Dreyer et al., 2003).

Table 3.3 The damage categories in Eco-Indicator 99 (PRé, 2000).

Damage categories	Impact categories
Human health	Climate change
	Ozone layer depletion
	Carcinogenic effects
	Respiratory effects
	Radiation
Ecosystem quality	Ecotoxicity
	Acidification
	Eutrophication
	Land use
Resources	Fossil fuels
	Minerals

Results and discussion

LCA results of the scenarios

Table 3.4 shows the TRACI results for Scenario 1, where it can be observed that by producing 1 kg of structural bio-adhesive results in 12.18 kg CO_2-eq global warming air emission. With respect to acidification potential, 5.39 kg H+ moles-eq /FU of acid air is produced. Other TRACI impact results are shown below. It should be noticed that human toxicity with respect to cancer effects is 4.21E-09 CTUh/FU, and result here is relatively lower than that for urea-formaldehyde adhesive's production processes (3.42E-07 CTUh/FU human toxicity, cancer effect), indicating that this bio-adhesive's production process is less harmful to human health. Fig. 3.10 illustrates the global warming potential (GWP) for each process.

Table 3.5 shows the TRACI results for Scenario 2, showing that 14.50 kg CO_2-eq of greenhouse gas emission is observed when producing 1 kg of structural adhesive, and the acidification potential and eutrophication potential are 5.48 kg H+ moles-eq /FU and 2.18E-03 kg N moles-eq /FU, respectively.

Table 3.4 TRACI results of Scenario 1 with mass allocation.

Impact method	**Result**
TRACI global warming [kg CO_2-eq/FU]	12.18
TRACI acidification [kg H+ moles-eq/FU]	5.39
TRACI eutrophication [kg N-eq/FU]	2.43E-03
TRACI ozone depletion air [kg CFC 11-eq/FU]	2.36E-11
TRACI smog air [kg O_3-eq/FU]	0.91
TRACI human health particulate air [kg PM 2.5-eq/FU]	5.18E-03
TRACI human toxicity, cancer [CTUh/FU]	4.21E-09
TRACI human toxicity, non-cancer [CTUh/FU]	2.68E-07

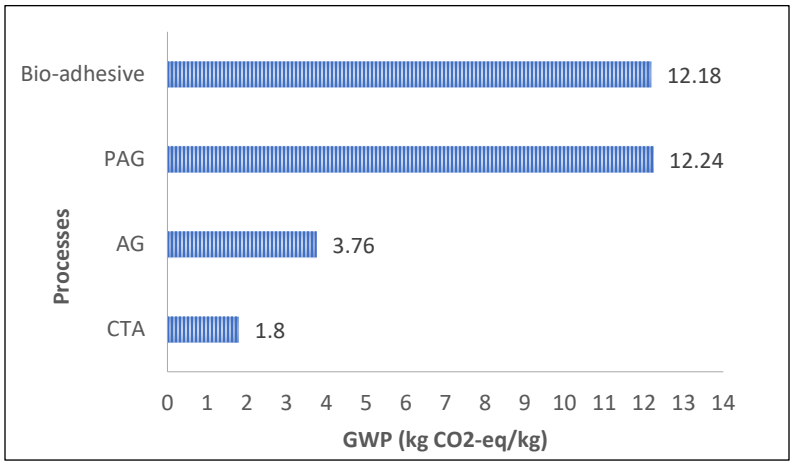

Figure 3.10 Global warming potential of the structural bio-adhesive production process with mass allocation.

Table 3.5 TRACI result of Scenario 2.

Impact method	**Result**
TRACI global warming [kg CO_2-eq/FU]	14.50
TRACI acidification [kg H+ moles-eq/FU]	5.48
TRACI eutrophication [kg N-eq/FU]	2.18E-03
TRACI ozone depletion air [kg CFC 11-eq/FU]	9.20E-11
TRACI smog air [kg O_3-eq/FU]	0.97
TRACI human health particulate air [kg PM 2.5-eq/FU]	5.37E-03
TRACI human toxicity, cancer [CTUh/FU]	6.35E-09
TRACI human toxicity, non-cancer [CTUh/FU]	2.88E-07

Scenario comparisons

Fig. 3.11 and Fig. 3.12 show a comparison of TRACI results between Scenario 1 and Scenario 2. As expected, Scenario 2 has larger environmental impact than Scenario 1 in all aspects. More greenhouse gas (GHG) were generated from Scenario 2 (14.50 kg CO_2-eq/FU) than Scenario 1 (12.18 kg CO_2-eq/FU) (difference = 19%). The greater GHG emission in Scenario 2 is largely produced from the petroleum refinery. Differences less than 5% were observed in other TRACI environmental impact categories such as acidification potential (AP), eutrophication potential (EP), and ozone depletion potential (ODP), smog air, etc. Fig. 3.12 shows the results after natural log transformation. Because there are only slight difference of these impact categories between the two scenarios, the results after natural log transformation are somewhat clearer.

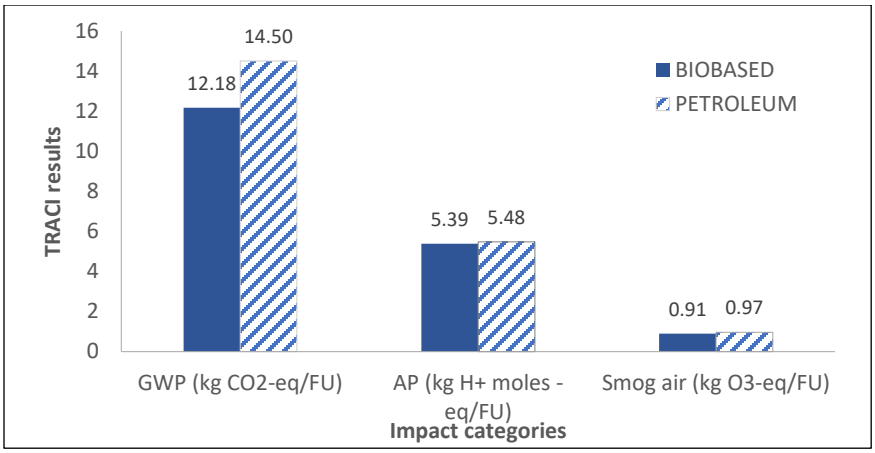

Figure 3.11 Comparison of the TRACI results between the two scenarios (part a).

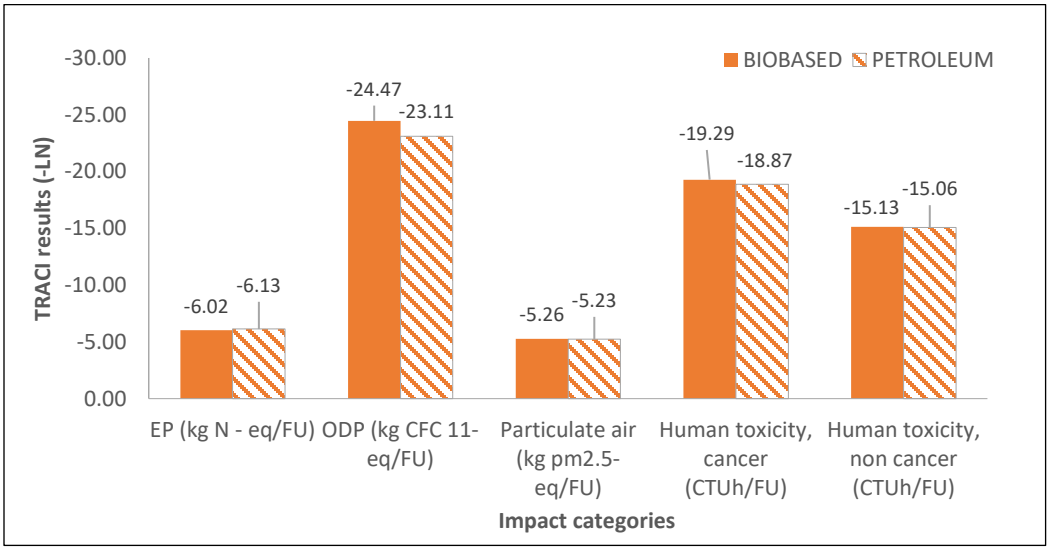

Figure 3.12 Comparison of the TRACI results between the two scenarios (part b).

Fig. 3.13 illustrates the Eco-Indicator 99 (EI 99) results for the two scenarios. It is found that resource depletion is almost 50% larger in Scenario 2 (petro-glycerin scenario) than Scenario 1. The environmental impacts on human health in Scenario 2 is also 13% higher than for Scenario 1, indicating that biobased material is less harmful to humans. The impact on ecosystem quality is 6% higher for Scenario 2 than for Scenario 1. With respect to overall environmental performance, Scenario 2 has a higher impact score (8.4 pts) than Scenario 1 (6.4

pts), a difference of 32%, a similar result to other work in this field. In 2014, McDevitt and Grigsby did a comparison of bio-adhesives and petro-adhesives used in fiberboard production in New Zealand, where they found that the overall environmental impact of biobased materials has a 22% lower EI 99 result than for petrochemicals (McDevitt and Grigsby, 2014).

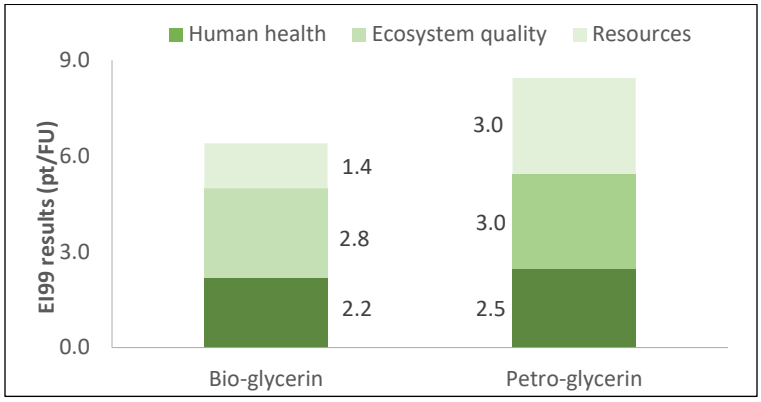

Figure 3.13 Eco-Indicator 99 results of the two scenarios in structural bio-adhesive production.

Energy consumption

The energy consumption results are shown in Fig. 3.14. It is found that the energy consumed in Scenario 2 (279 MJ/FU) is nearly 12% higher than Scenario 1 (248 MJ/FU). The result suggests that the petroleum refinery process requires more energy than biodiesel production process.

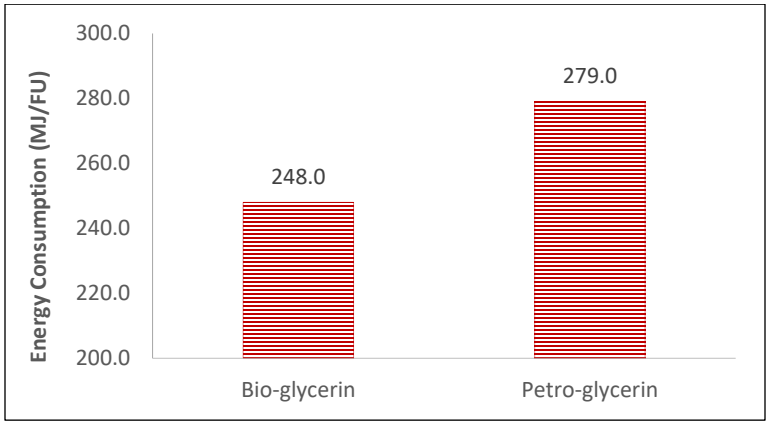

Figure 3.14 Energy consumption of the two scenarios.

Allocation methods comparison

The comparison of various allocation methods was conducted for Scenario 1 only. We focused the impact assessment result on global warming potential (GWP) since this aspects attracts the most attention concerning environmental effect. Fig. 3.15 shows the TRACI results on the GWP of the three allocation methods, showing that the economic allocation method leads to the lowest impact (11.62 kg CO_2-eq/FU), and the energy allocation method has the highest environmental impact (13.70 kg CO_2-eq/FU).

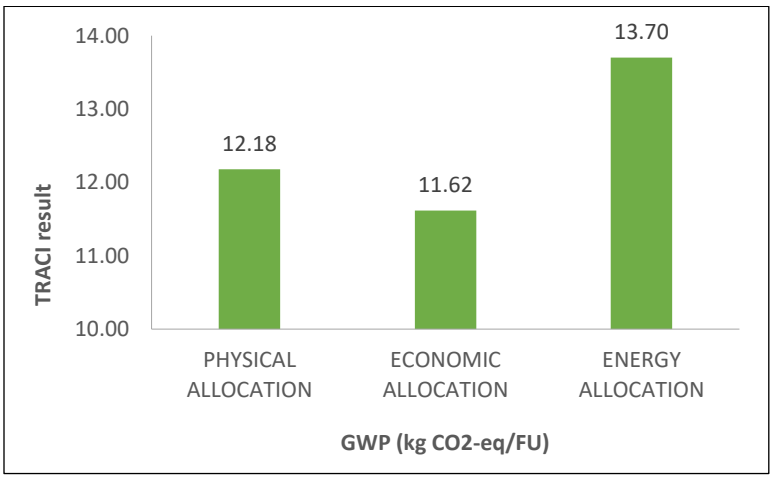

Figure 3.15 Comparison among three allocation methods by TRACI method.

As for the EI-99 results (Fig. 3.16), the energy allocation method has the highest overall environmental impact (7.3 pts/FU) compared with the other two methods (6.4 pts/FU for the mass allocation method and 6.1 pts/FU for the economic allocation method). With respect to human health impact, all allocation methods tends to have similar results. For ecosystem quality and resource impact, mass allocation result is slightly higher than the economic allocation result (2.8 pts/FU vs. 2.7 pts/FU for ecosystem quality and 1.4 pts/FU vs. 1.3 pts/FU for resources), but results from the energy allocation method are much higher (3.1 pts/FU of ecosystem quality and 1.8 pts/FU of resources).

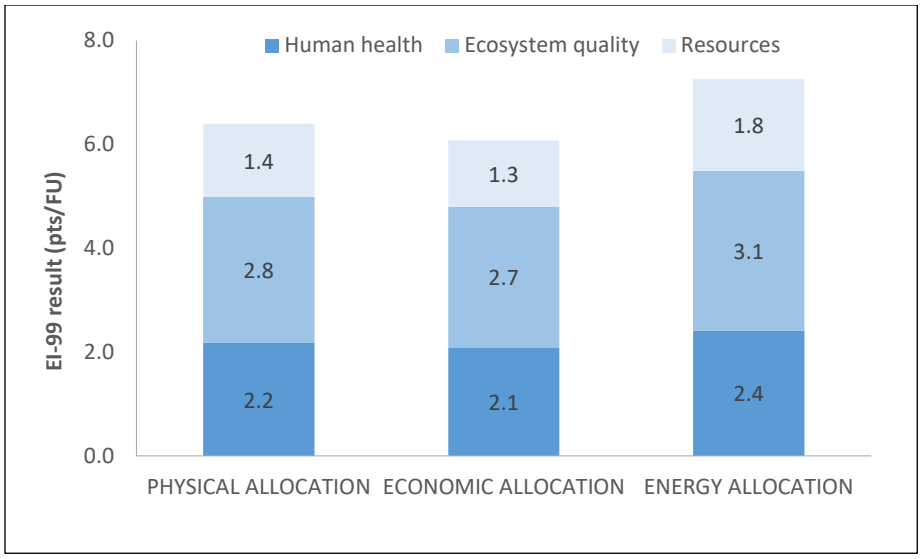

Figure 3.16 Comparison among three allocation methods by EI-99 method.

The highest impact results for the energy allocation method could be explained by the large difference between biodiesel and glycerol costs (23.59 $/gal vs. 46 ¢/gal), and relatively close LHVs between them (33.66 MJ/kg vs. 25.3 MJ/kg). Compared to mass allocation methods, the energy allocation factor is 3.3 times larger, while the economic allocation factor accounts for only 0.15 of the mass allocation factor.

Sensitivity analysis

Sensitivity analysis has been carried out to determine the critical factor in the bio-adhesives' production process (Scenario 1 only). As suggested in the literature, the electricity source, the production yield and the transportation distance could be important factors in terms of GHG emissions. Thus, three sensitivity analysis were separately conducted on these three factors.

Fig. 3.17 shows the sensitivity analysis results for electricity sources. The original GHG emission in Iowa was 12.18 kg CO_2-eq/MJ of electricity and, as mentioned in *Methods*, the electricity sources in Iowa were composed of fossil fuels by nearly 60%. If the electricity comes

from 100% coal, the GHG emission could increase to 20.58 kg CO_2-eq/MJ of electricity, while if the electricity is 100% clean (from biomass), the GHG emission is reduced to 2.93 kg CO_2-eq/MJ of electricity. While the increase in GHG emission is almost 40%, it could be decreased by more than 70%, implying that replacing the energy source with renewable energy could greatly decrease the environmental impact.

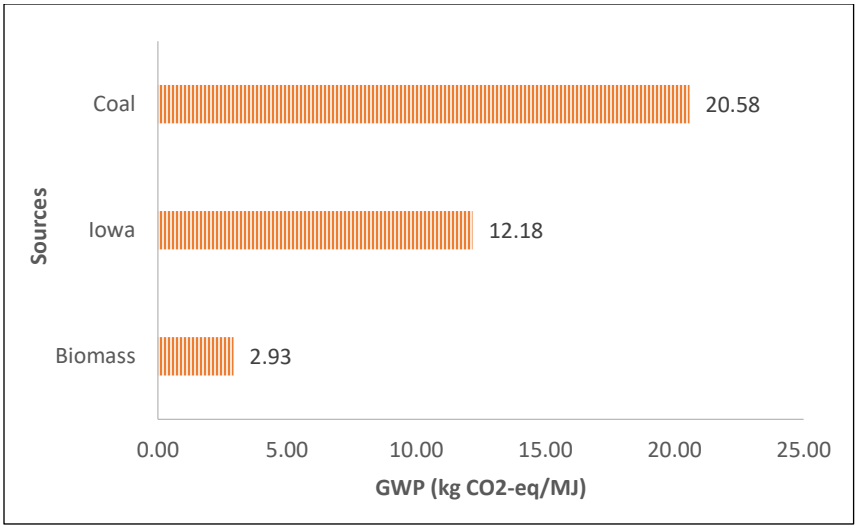

Figure 3.17 Sensitivity analysis on electricity sources.

The second sensitivity analysis was related to the product yield (Fig. 3.18). In this study, it has been assumed that, based on the laboratory result, the final product yield is 100%. However, when the bio-adhesive production process is scaled up to commercial level, the product yield could decrease by 5%, or even 10%. We therefore estimated the GHG emission on these situations, and found that the GHG emission increase by nearly 20% (14.65 kg CO_2-eq/kg of bio-adhesive) if the product yield is 95%. If the product yield decreases to 90%, the GHG emission increases only by 5%, again based on a 95% yield. These findings suggest that there will be a large growth in GHG emission once product yield decreases.

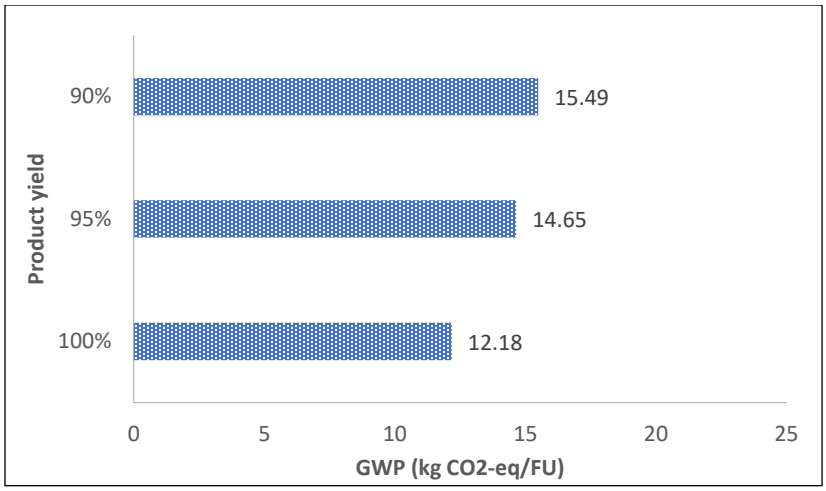

Figure 3.18 Sensitivity analysis on production yield.

The third sensitivity analysis was related to the transportation distance (Fig. 3.19). The transportation distance is assumed as 50 miles from the production plant, within the state of Iowa. The transportation distance may result in changes of GHG emission due to its requirement for usage of diesel. In this study, we changed the distance to 500 miles and 1,000 miles to represent future market requirement, and surprisingly found that altering the transportation distance resulted in only a small effect with respect to GHG emission, ranging from 12.18 kg CO_2-eq to 12.59 kg CO_2-eq when producing 1kg of structural bio-adhesive.

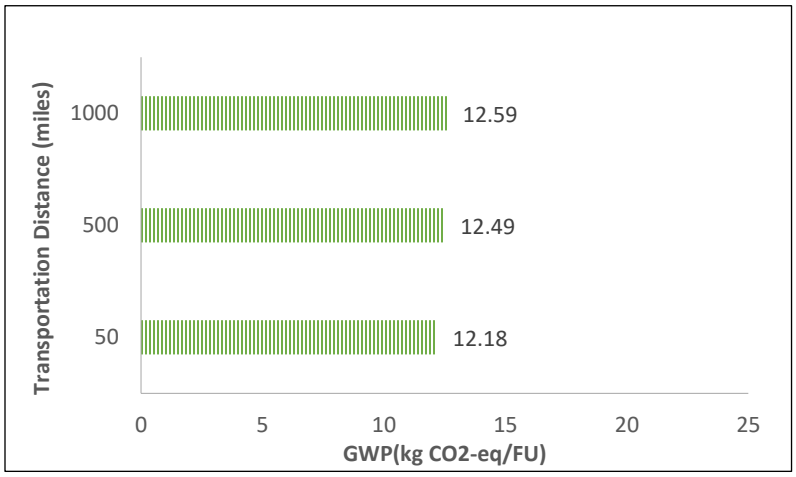

Figure 3.19 Sensitivity analysis on transportation distance.

Conclusions

In this study, life cycle assessment (LCA) was conducted to quantify the environmental impact of the structural bio-adhesive production process. As quantified in GaBi, the global warming potential (GWP) could reach 12.18 kg CO_2-eq when producing 1 kg of structural bio-adhesive; the energy required for producing 1 kg of structural bio-adhesive is 248 MJ. When bio-glycerol is replaced with petro-glycerol, the overall environmental impact will increase by around 23%, and it also requires higher energy consumption. The choice of allocation methods has some effect on the environmental impact. It is found adopting the energy allocation method results in more impact for the structural bio-adhesive production process. The sensitivity analysis results suggest that the structural bio-adhesive production process is most highly sensitive to electricity sources, followed by product yield, while there is only little sensitivity to the overall process to the factor of transportation distance. Due to the data incompleteness and uncertainty associated with the study, future study may be required to further explore the environmental impact, including social impact, of this structural bio-adhesive process.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This study was funded by the National Institute of Food and Agriculture of the United States Department of Agricultural, under the project number 214-38202-22318.

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CHAPTER 4. TECHNO-ECONOMIC ANALYSIS OF THE PRODUCTION PROCESS OF STRUCTURAL BIO-ADHESIVES DERIVED FROM GLYCEROL

A paper submitted to *Journal of Cleaner Production.*

Abstract

With increasing environmental concerns with respect to the petroleum-based adhesives production process, bio-based adhesives have been explored as a promising replacement. The purpose of this paper was to explore the economic feasibility of structural bio-adhesives made from glycerol, a byproduct of biodiesel production. SuperPro Designer v9.5 software was employed to perform the techno-economic analysis (TEA). Several key parameters were analyzed, such as total capital investment, annual operating cost and revenue. It was found that the unit production price of structural bio-adhesives ($2.45 /kg) was compatible with that for structural adhesives in the current market. Three different scenarios were built to investigate the worst-case scenario and the best-case scenario associated with this production process. Sensitivity analysis was also performed to evaluate the key parameters significantly influencing the economic results. In this study, material cost was determined to be the most significant factor throughout the production process. Discounted cash flow (DCF) analysis was conducted to explore the influence of the time value of money. The minimum selling price (MSP) obtained when net present value (NPV) equals zero was $3.11 /kg for this bio-adhesive production process. Underlying issues and areas needed for improvement were also discussed in this study.

Keywords

Techno-economic analysis (TEA); Structural bio-adhesives; Glycerol; Sensitivity analysis; Cash flow analysis.

Introduction

The current global economy is highly dependent on crude oil processing since it provides many raw materials for manufacturing commercial products. As estimated by the U.S. Energy Information Administration (EIA), the average 2016 crude oil production in the lower U.S. 48 states was 8.39 million barrels per day (b/d) (U.S. EIA, 2017). The lighter fractions in crude oil refinery, such as propylene, have lower density and lower specific gravity, and light crude oil can be processed into multiple products, e.g., plastics and binding agents (Nitzsche et al., 2016). However, because of the non-renewable and exhaustible characteristics of fossil fuels and the increasing environmental concerns, i.e. global warming problem, numerous efforts have been made to reduce the dependency of petroleum production on the global economy (Bardhan et al., 2015).

Adhesives have been used for thousands of years with wide application in fields like wood production, paper bonding, automotive, and aerospace. As reported by *Grand View Research*, the size of the worldwide industrial adhesive market was 9,400 kilotons in 2014 (Grand View Research, 2017), and it has been forecast by *Freedonia* that the U.S. demand for adhesive will increase by 2.8% each year until 2019, representing a value of $12.8 billion (Freedonia, 2017).

Adhesive can be categorized in many ways. For example, on the form of cross-linked molecules, it can be divided into thermosetting or thermoplastic. With respect to flexibility, adhesives can be divided into rigid or elastomeric categories. Another way to classify the adhesive is according to their loading capabilities, where they can be categorized as structural and non-structural (Petrie, 2000).

Structural adhesive is one of the largest groups used in numerous industrial processes; it is normally employed in high-strength, permanent applications. As forecast by *Markets and*

Markets, the global structural adhesive market will reach $12.74 billion by 2021 (Markets and Markets, 2017).

Biobased adhesives are those derived from renewable resources such as crops and crop residues, by-products of bio-renewable manufacturing, or from animal sources (Imam et al., 1999). Bio-adhesives from renewable resources are mostly structural bio-adhesives, the unique macromolecular features of structural bio-adhesives make them quite attractive for use in the fields of consumer products, biomedical devices, bioplastics and wood adhesives (Smith, 2005).

A synthesized structural biobased adhesive is usually formulated as polymeric resins. Typical resin families used in formulating structural bio-adhesives include epoxy adhesive, resorcinol resin, urea formaldehyde resin, phenolic resin, polyesters, and modified acrylic adhesive, each with its unique characteristics.

Epoxy adhesive is the most widely used structural adhesive because it exhibits an excellent ratio of strength to weight (Yasuhisa and Yasuhisa, 2017). Such adhesives are probably the most versatile type because their modification process is relatively simple and, as a consequence, they can achieve widely varying properties (Petrie, 2000). However, epoxy adhesives are vulnerable to moisture attack due to hydrophilic groups that may significantly degrade epoxy adhesive mechanical properties (Loh et al., 2005).

Modified acrylic adhesive has the advantage of rapid cure and high strength; it is often used in high-speed automated assembly operations (Petrie, 2000). This type of adhesive uses acrylate acid as a monomer for polymerization.

More than 50% of the polymer production process is based on free radical polymerization techniques that are widely used because of their robustness and capability for producing materials with unique characteristics. However, the free radical polymerization process produces

non-biodegradable materials and is largely dependent on fossil fuels (Semsarilar and Perrier, 2010).

In this study, the reversible addition-fragmentation chain transfer (RAFT) polymerization process is chosen. This process, first reported in the late 1990s, is one of the living radical polymerization (LRP) techniques, and also a free radical polymerization process. The best-known characteristic of the LRP technique is that it can continue the polymerization process even when the initial feed is exhausted, so that won't terminate the polymerization process (Semsarilar and Perrier, 2010). Over the past decades, the RAFT polymerization process has become one of the most popular techniques because of its versatile synthetic characteristics. For example, this process can be applied to most vinyl monomers, and can be compatible under a variety of conditions (Zhang et al., 2015). It has also been proven a useful technique for synthesizing hydrophilic polymers (Lowe and McCormick, 2007).

In general, the RAFT polymerization process starts with an initiation step aimed at creating a radical. The radical ($P_m^{\cdot}$) is reversibly added to the chain transfer agent (CTA) to create a reinitiating group ($R^{\cdot}$). A chain transfer agent (CTA) or a RAFT agent is a critical component in the RAFT polymerization process, comprising the key to successful polymerization, following which $R^{\cdot}$ reinitiates the polymerization process. Following re-initiation, the main equilibrium RAFT polymerization process is dominant in growing the polymer chain until a termination reaction occurs (Semsarilar and Perrier, 2010).

The RAFT polymerization process can be carried out under environmental-friendly conditions, such as water-based solvent (Lowe and McCormick, 2007) and ionic liquids (Shakraborty et al., 2014). Moreover, the RAFT polymerization process can be applied to renewable resources, and both organic and inorganic renewable materials can be polymerized via

RAFT polymerization (Boyer et al., 2009). However, a number of renewables being used to manufacturing products are at present in low supply, mostly because economic value is the main driving factor of industry, and renewables have found it difficult to achieve economic parity compared with petroleum goods (Hernandez et al., 2014). In 2013, Cochran et al. broadened the RAFT polymerization application by creating novel thermoplastic homopolymer and block copolymers derived from plant oil or animal oil (Cochran et al., 2014).

Techno-economic analysis (TEA) is a process-modeling form of study for simulating the production process. TEA includes both technical parameters and economic factors in project analysis (Chau et al., 2009). TEA starts with material and energy balance, and cost configuration is then conducted to assess a product's economic feasibility. Literatures on TEA are extensively explored in the area of renewable energy, and in the realm of biochemical production, TEA is substantially used for evaluating economic feasibility of a production process.

This TEA research is focused on a novel production process of structural bio-adhesive developed by Iowa State University researchers. To the authors' knowledge, no previous TEA work has been done on this unique bio-adhesive process. The main objectives of this study are to model the structural bio-adhesive, specifically modified acrylic bio-adhesive, production process and to evaluate the economic feasibility of this production process. The modeling process of the structural bio-adhesive will be described in the *Methods* section; the economic analysis results for the model, including overall economic performance, sensitivity test, and discounted cash flow analysis, will be subsequently analyzed. Underlying issues associated with the production process will also be discussed.

Methods

This section will describe the method of performing this TEA study, including the modeling approach, the economic analysis, the uncertainty analysis, and the discounted cash

flow (DCF) analysis. The production process of the structural bio-adhesive was modeled in five scales: 1 t/d, 2 t/d, 5 t/d, 10 t/d, and 40 t/d. The largest scale (40 t/d) was chosen based on a real industrial adhesive production plant shown in *Phoenix Equipment Corporation* (Phoenix Equipment Corporation, 2017).

Process design description

SuperPro Designer v9.5 software (*Intelligen Inc.*, Cambridge, Massachusetts, USA) was used to perform computer modeling of the selected production process, and the data used in modeling this structural bio-adhesive production process was collected from Iowa State University (ISU) laboratory results. A simplified flowchart of the overall structural bio-adhesive production process is depicted in Fig. 4.1.

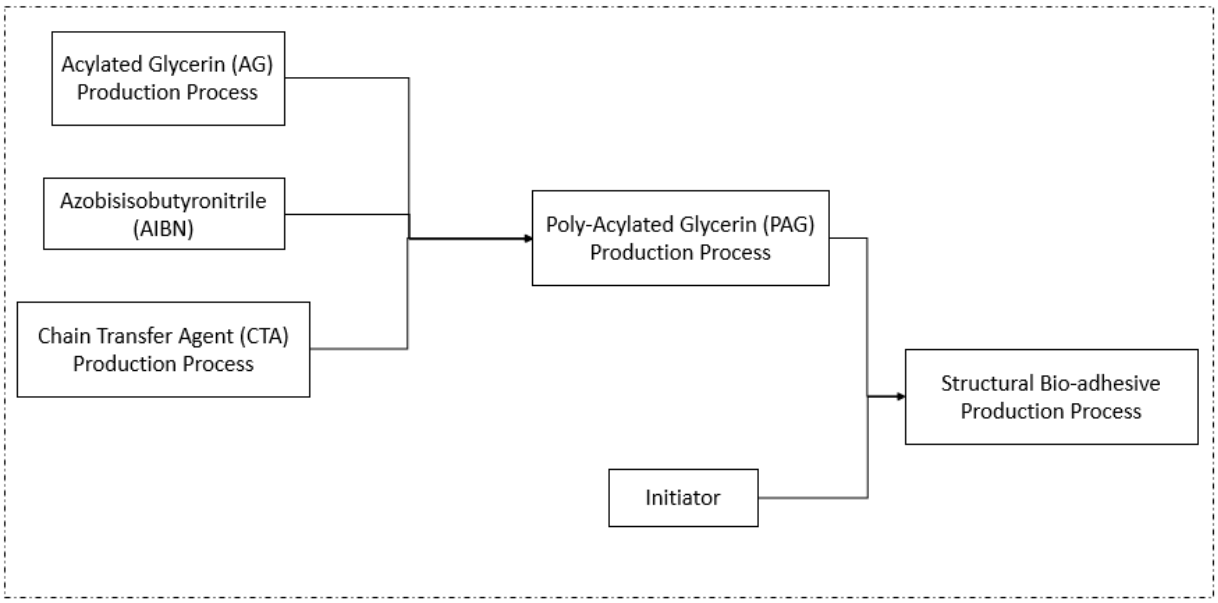


Figure 4.1 Simplified overall flowchart of the structural bio-adhesive production process.

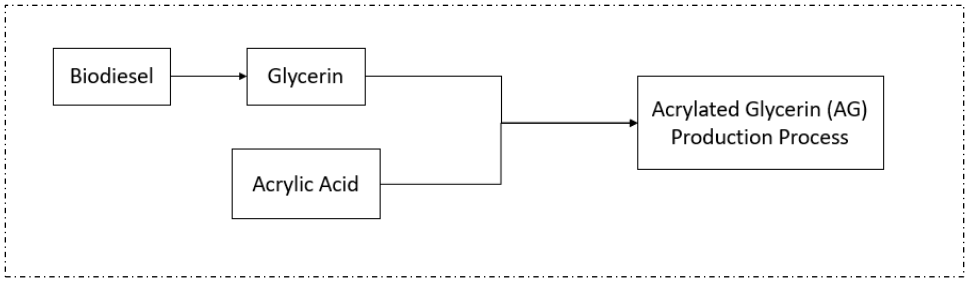
The chosen production process begins with acrylic acid and bio-based glycerin from the biodiesel industry. Acrylated glycerin (AG) is produced through Fisher esterification of these

two materials, as shown in Fig. 4.2 (A), with Amberlyst 15 and phenothiazine (PTZ) adopted as catalysts during esterification. This process is conducted under mild temperature and atmospheric conditions.

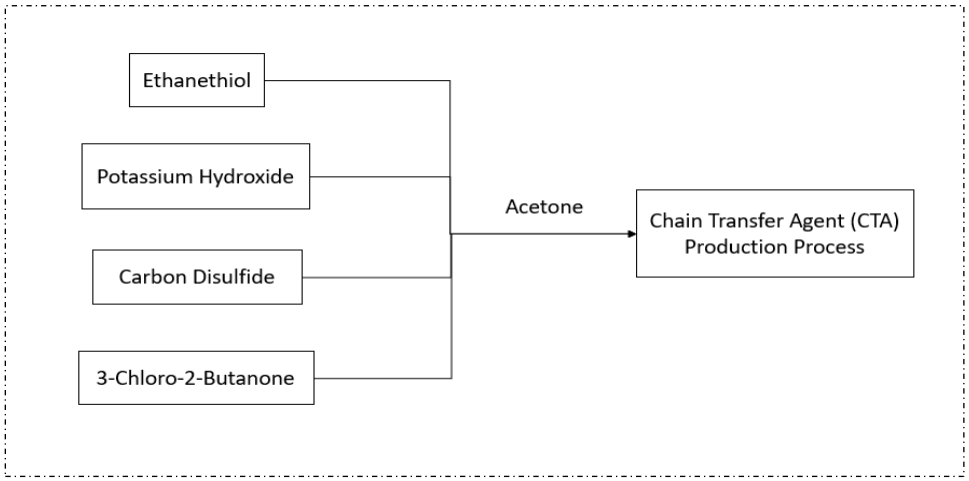
After the AG is produced, the RAFT polymerization process begins as a two-step process with the initial process one of producing AG monomer. The second step is to produce polymerized acrylated glycerin (PAG). As previously discussed, the RAFT agent or the chain transfer agent (CTA) is the most important component in the polymerization process. Fig. 4.2 (B) shows the materials used to produce the CTA. Ethanethiol is neutralized with KOH for 30 minutes, then CS_2 is reacted with a pH neutral solution for 30 minutes, 3-chloro-2-butanone is added afterward, and the mixture allowed to stir for 30 minutes. Acetone is used as the buffer solution during the CTA production, and is recycled for continuous production with a recycle rate of 97%. Potassium chloride (KCl) is produced as a byproduct of this process. The CTA is purified through the distillation column, and after purification, the CTA is reacted with AG and Azobisisobutyronitrile (AIBN) to perform RAFT polymerization. The reaction proceeds at 70°C for 4 hours. At the end of the RAFT polymerization, water is added to precipitate the polymer.

After polymerization process, an initiator (4, 4’-azobis) is added to produce the structural bio-adhesive preserved in liquid form.

Computer models generated from SuperPro Designer are shown in Fig. 4.3, Fig. 4.4, and Fig. 4.5.



(A)



(B)

Figure 4.2 Flowcharts of (A) acrylated glycerin (AG) production process and (B) chain transfer agent (CTA) production process.

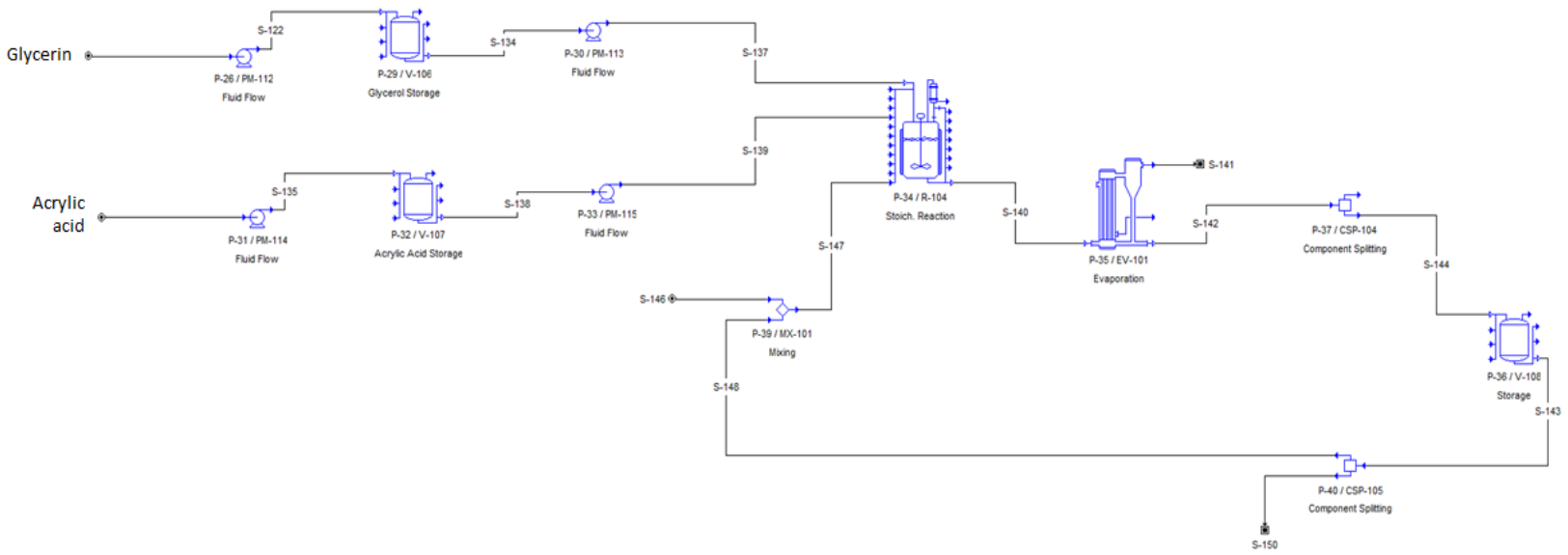


Figure 4.3 Computer model built in SuperPro Designer software (AG production process).

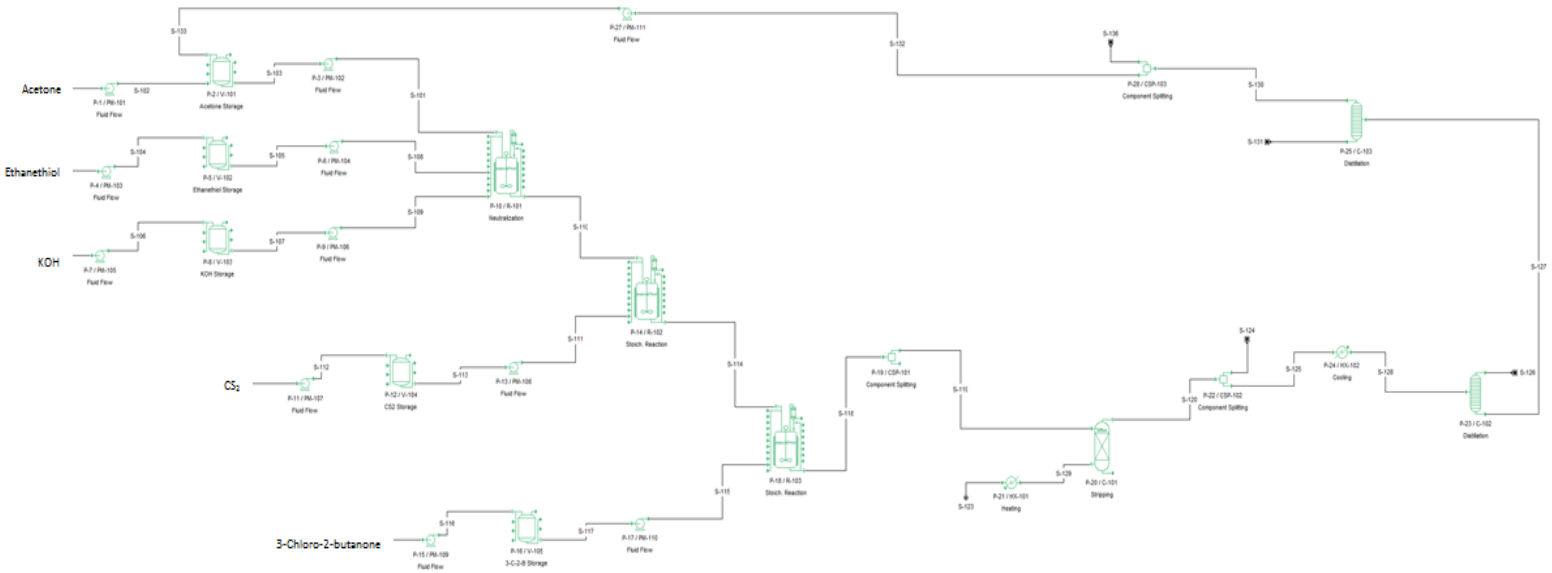


Figure 4.4 Computer model built in SuperPro Designer software (CTA production process).

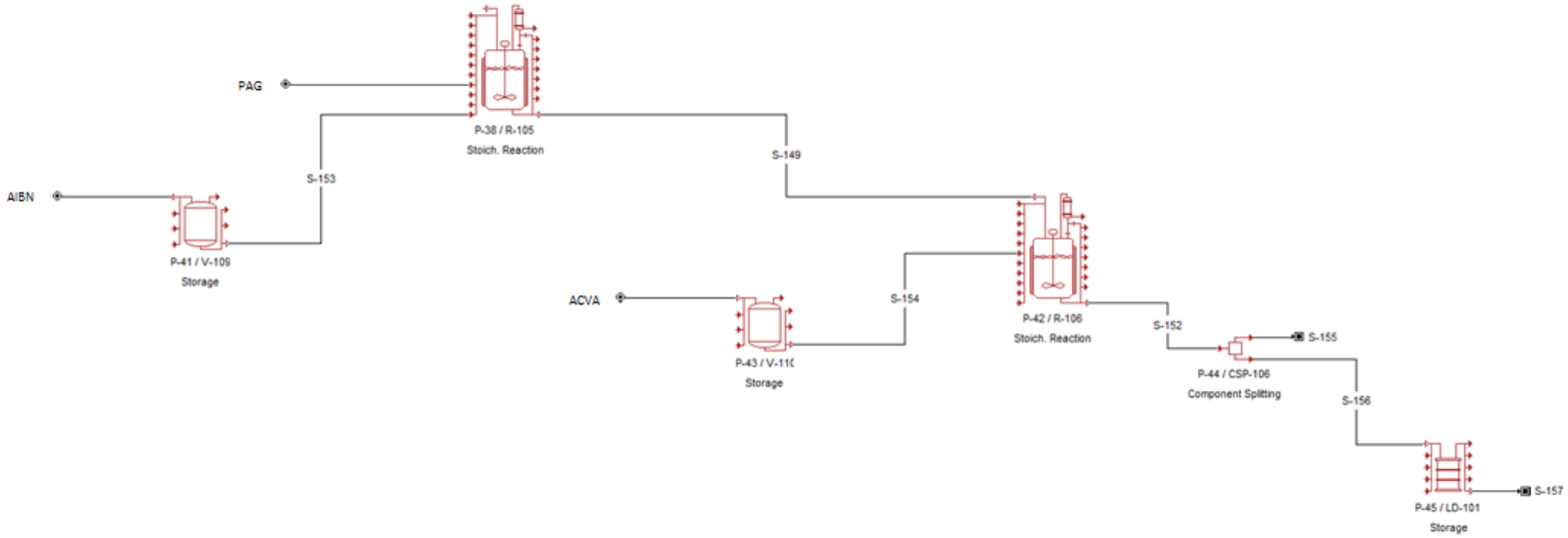


Figure 4.5 Computer model built in SuperPro Designer software (RAFT polymerization and adhesive production process).

Economic analysis

The Association for the Advancement of Cost Engineering International (AACE International) has defined five types of estimates in terms of expected accuracy levels. This TEA research study is an order-of-magnitude estimate study, with an expected accuracy between +50% and -30% (AACE, 2017). Data from the Iowa State University's laboratory research, literatures, and technical reports have been used to estimate facility costs for this production pathway. The results from the SuperPro Designer v9.5 computer model have been used in economic feasibility evaluation.

Total capital investment (C_{TCI}) can be broken down into three parts: direct fixed capital cost (C_{DFC}), working capital (C_W), and startup costs (C_S). Working capital is the money invested in getting a plant into productive operation (Ulrich, 1984); Start-up costs are the costs to make the transition from construction to operation (Humphreys, 2005). It is assumed that this structural bio-adhesive production plant would be located in central Iowa. The construction time was set to 24 months, and the assumed start-up time was 6 months. The online time was assumed to be 329 days per year (7,896 h/y), equivalent to a capacity factor of 90% and assumed plant life was 15 years. The assumptions for total capital cost investment (C_{TCI}) are listed in Table 4.1. SuperPro Designer v9.5 software was employed to estimate the equipment purchase costs, and other assumptions were obtained from Peters et al. (Peters et al., 2015).

Total capital cost investment (C_{TCI}) is calculated using Eq. 4.1.

$$C_{TCI} = C_{DFC} + C_W + C_S \quad \text{(Eq. 4.1)}$$

Table 4.1 Assumptions used to model the total capital cost investment (C_{TCI}).

Parameter	Assumption	Source
1. Direct fixed capital cost (C_{DFC})	$C_{DC} + C_{IC} + C_{OC}$	
1) Direct cost (C_{DC})		
Equipment purchase cost (C_{PC})		SuperPro Designer database
Piping	0.68* C_{PC}	Peters et al., 2015
Instrumentation	0.50* C_{PC}	Peters et al., 2015
Insulation	0.03* C_{PC}	Peters et al., 2015
Electrical facilities	0.30* C_{PC}	Peters et al., 2015
Building	0.45* C_{PC}	Peters et al., 2015
Yard improvement	0.20* C_{PC}	Peters et al., 2015
Auxiliary facilities	0.55* C_{PC}	Peters et al., 2015
Installation	0.55* C_{PC}	Peters et al., 2015
Land	0.08* C_{PC}	Peters et al., 2015
2) Indirect cost (C_{IC})		
Engineering	0.30* C_{DC}	Heinzle, 2006
Construction	0.35* C_{DC}	Heinzle, 2006
3) Other cost (C_{OC})		
Contractor's fee	0.06*($C_{DC} + C_{IC}$)	Peters et al., 2015
Contingency	0.08*($C_{DC} + C_{IC}$)	Peters et al., 2015
2. Working capital (C_W)	0.15* C_{DFC}	Ulrich, 1984
3. Start-up and validation cost (C_S)	0.10* C_{DFC}	Peters et al., 2015

Annual operating cost (C_{AOC}) is divided into four classifications: materials cost (C_M), utility cost (C_U), labor cost (C_L) and facilities cost (C_F), and underlying economic assumptions listed in Table 4.2. Material costs were obtained from retailer websites, as detailed in sources. The electricity price was collected from a U.S. Energy Information Administration (EIA) electric power monthly report (U.S. EIA, 2017). The costs for steam and process water were gathered from the SuperPro Designer v9.5 software database. Operating labor cost was assumed at 20% of the annual operating cost (C_{AOC}) (Peters et al., 2015), and supervisory labor cost was not considered in this study. Other assumptions were obtained from Peters et al. (Peters et al., 2015). Wastewater treatment process costs, research and development (R&D) costs, and distribution and marketing costs have not been considered. Since the depreciation method chosen in this study was the straight-line method, the recovery period for the manufacture of chemicals and allied products is 9.5 years (Department of Treasury, 2017). The salvage value of the purchased equipment is assumed to be zero (Turton et al., 2012).

Annual operating cost (C_{AOC}) is calculated using Eq. 4.2.

$$C_{AOC} = C_M + C_U + C_L + C_F \quad \text{(Eq. 4.2)}$$

Table 4.2 Assumptions used to model the annual operating cost (C_{AOC}).

Parameter	Assumption	Source
1. Materials cost (C_M)		
Glycerol	1.04 $/kg	Landress, 2017
Acrylic acid	0.90 $/kg	Molbase, 2017
Phenothazine (PTZ)	11.30 $/kg	Molbase, 2017
Amberlyst 15	104.00 $/kg	Molbase, 2017
Ethanethiol	5.48 $/kg	Molbase, 2017

Table 4.2. (continued)

Parameter	Assumption	Source
Carbon disulfide	1.37 $/kg	Molbase, 2017
3-chloro-2-butanone	35.22 $/kg	Molbase, 2017
Acetone	0.10 $/kg	Molbase, 2017
Azobisisobutyronitrile (AIBN)	5.81 $/kg	Molbase, 2017
4, 4'- Azobis	565.00 $/kg	Molbase, 2017
Potassium hydroxide (KOH)	1.05 $/kg	Molbase, 2017
2. Utilities cost (C_U)		
Electricity	5.08 cents/kWh	U.S. EIA, 2017
Steam	12.00 $/MT	SuperPro Designer
Process Water	0.05 $/MT	database
3. Labor cost (C_L)		Peter et al., 2015
4. Facility cost (C_F)		
Maintenance	0.02* C_{PC}	Peter et al., 2015
Depreciation	Straight-line method	Department of Treasury, 2017
Insurance	0.01* C_{DFC}	Peter et al., 2015
Tax	0.02* C_{DFC}	Peter et al., 2015
Plant overhead	0.50* C_L	Peter et al., 2015

In this study, structural bio-adhesive, i.e., modified acrylic bio-adhesive, is the main product, and potassium chloride (KCl) serves as a byproduct. The selling price of modified acrylic bio-adhesive is obtained from the U.N. Comtrade Database (U.N. Comtrade, 2017). The KCl selling price was obtained from the World Bank (World Bank, 2017). The gross profit (Eq. 4.3), net profit (Eq. 4.4), return on investment (ROI) (Eq. 4.5), payback time (Eq. 4.6), and unit production cost (Eq. 4.7), have been calculated based on revenues.

$$Gross\ profit\ (\$) = Revenues - C_{AOC} \quad \text{(Eq. 4.3)}$$

$$Net\ profit\ (\$) = Gross\ Profit - Taxes + Depreciation \quad \text{(Eq. 4.4)}$$

$$Return\ on\ investment\ (\%) = \frac{Net\ profit}{Total\ investment} \times 100 \quad \text{(Eq. 4.5)}$$

$$Payback\ times\ (years) = \frac{Total\ investment}{Net\ profit} \quad \text{(Eq. 4.6)}$$

$$Unit\ production\ cost\ (\$/kg) = \frac{Annual\ total\ investment}{Unit\ reference\ flow} \quad \text{(Eq. 4.7)}$$

Uncertainty analysis

Uncertainty analysis was performed to predict the economic factors' influence on profitability. Scenario analysis is one way to quantify uncertainty, and when performing scenario analysis the best-case scenario and worst-case scenario are compared with the base scenario (Turton et al., 2012). In this study, a plant scale of 40 t/d was selected as the base-case scenario because it was the closest scale to actual industrial size. Three scenario analyses were performed in this study: 1) the total capital investment (C_{TCI}) varying over the range between +50% and -30%; 2) the structural bio-adhesive selling price varying over the range of ± 50%; 3) the comparison of glycerol sources, one from a biodiesel product plant, the other from a petroleum refinery.

The second method for performing uncertainty analysis is sensitivity analysis, used to investigate potential variation in the product value due to input variable variation (Saltelli et al., 2008). In this study, several variables were chosen based on their potential impact on product value.

Discounted cash flow (DCF) analysis

Discounted cash flow analysis was carried out by considering the time value of money. All cost results in this study, including the equipment cost and raw materials price, are presented in 2016 dollars. The discount rate is set as 10%, a commonly-used value in literatures (Li et al., 2015; Swanson et al., 2010), and the assumed plant life is 15 years. The assumed federal income tax rate is 40% (SmartAsset, 2017). The minimum selling price (MSP) for the structural bio-adhesive is calculated by setting net present value (NPV) to zero.

Results and discussion

A techno-economic analysis (TEA) of the production of structural bio-adhesive from glycerol was conducted in this study. The results include economic analysis, sensitivity analysis of critical factors, and a discounted cash flow analysis in terms of the economic indicators.

Economic analysis results

The total capital investments, annual operating cost, gross profits, and unit production costs are shown in Table 4.3. Not surprisingly, a larger plant scale requires higher total capital investment and higher annual operating cost, and in turn can provide higher gross profit and lower unit production cost.

The capital expenditures for the largest plant scale (40 t/d) were estimated to be $59 million. As discussed in *Methods*, the total capital investment (C_{TCI}) is composed of three major parts: direct fixed capital cost, working capital, and start-up cost. By breaking down the total capital investment (C_{TCI}), we found that the purchased equipment cost was nearly 10% of the C_{TCI}, occupying the largest part in the direct fixed capital cost (C_{DFC}) for all five scales.

Table 4.3 Economic analysis results of the structural bio-adhesive production process.

Scale (t/d)	Total capital investment ($)	Annual operating cost ($)	Gross Profit ($)	Unit Production Cost ($/kg)
1	44,603,776.80	2,947,563.86	- 1,524,069.96	16.07
2	46,395,405.79	4,119,712.69	- 220,952.94	9.79
5	49,068,071.66	6,056,651.79	1,291,697.28	5.06
10	51,354,873.90	9,830,618.28	4,908,613.04	3.60
40	59,032,598.63	32,137,092.09	26,825,307.77	2.45

The annual operating cost (C_{AOC}) is composed of material cost, utilities cost, labor cost and facilities cost. Utility consumption from SuperPro Designer v9.5 software and current raw materials marketing price are used to calculate the C_{AOC}. Fig. 4.6 illustrates that the material cost was the largest cost component in all five scales. This is consistent with most of the TEA studies that assert that raw materials frequently are the largest operating cost.

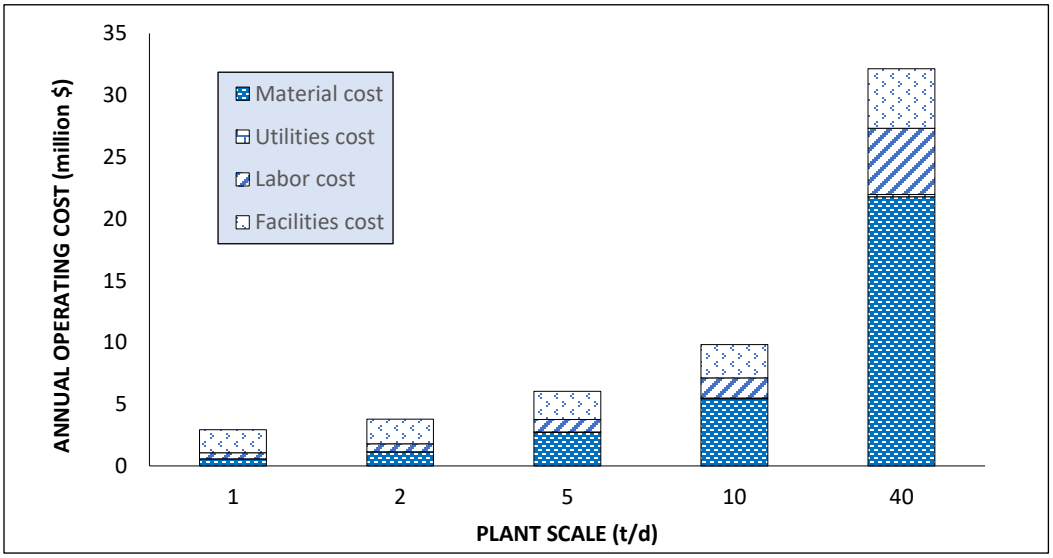


Figure 4.6 Annual operating cost ($) of the structural bio-adhesives in different scales.

The unit production cost ($/kg) of bio-adhesives for the five scales are shown in Fig. 4.7. In accordance with expectation, increasing plant scale will result in decreasing unit production price. The lowest unit cost for bio-adhesive obtained in this study is $2.45 /kg in the 40 t/d plant, and the payback time is 3.5 years. The trend line from the smallest plant to the largest one follows Eq. 4.8 with R^2= 0.95:

$$\text{Unit cost (\$/kg)} = 13.85 \times \text{Plant Scale (t/d)}^{-0.52} \quad \text{(Eq. 4.8)}$$

The lowest unit cost calculated in this study is slightly lower than the current marking price (U.N. Comtrade, 2017), possibly explained by the fact that the system boundary in this study is gate-to-gate; in other words, upstream and downstream processing costs were not used to calculate the unit production cost.

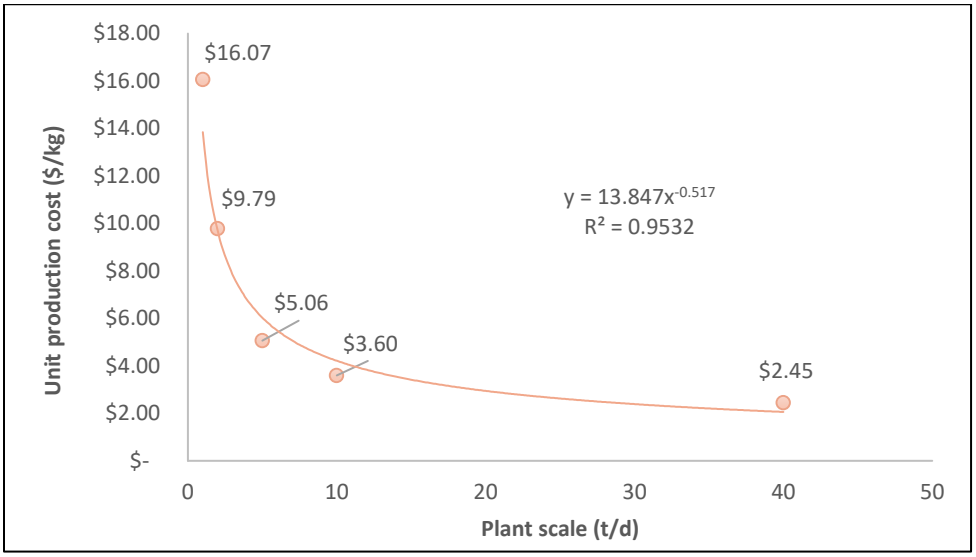


Figure 4.7 Unit production cost ($/kg) of the structural bio-adhesives in different scales.

Scenario analysis results

Scenario analysis on total capital investment (C_{TCI})

As mentioned in *Methods*, the uncertainty in this study ranges from +50% to -30%, as largely reflected in the total capital investment (C_{TCI}). Fig. 4.8 exhibits the three scenarios when

altering C_{TCI}. In the best-case scenario (-30%), the unit production cost of bio-adhesive is $2.33 /kg with a net profit of 17 million dollars, while in the worst-case scenario (+50%), the unit production cost is $2.64 /kg with a net profit of 16.1 million dollars. The difference in unit production cost between best-case scenario and the worst-case scenario is 11.74%. In terms of net profit and gross profit, the changes in C_{TCI} had little influence < 6%.

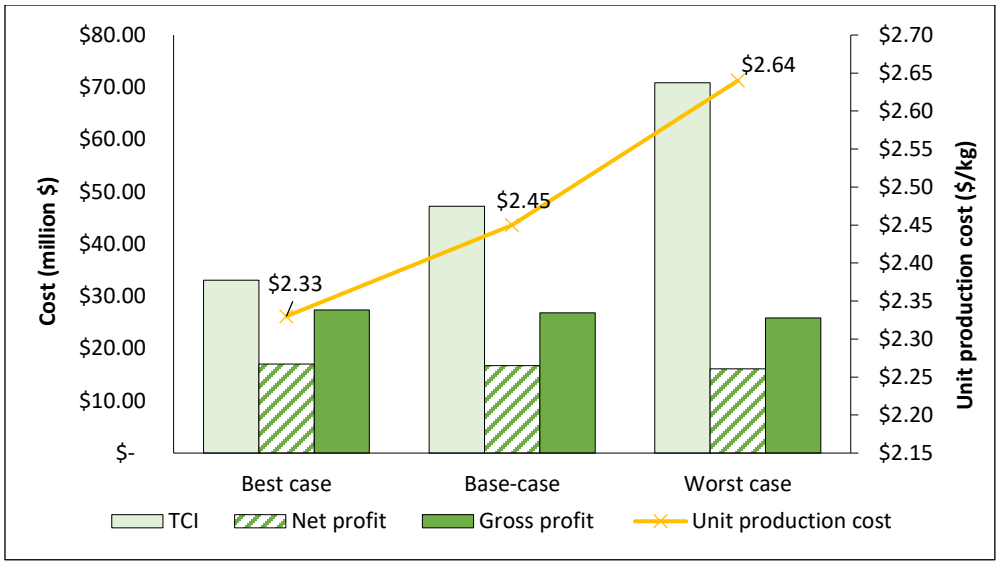


Figure 4.8 Scenario analysis results of total capital investment (C_{TCI}) for the structural bio-adhesive production process.

Scenario analysis on glycerol sources

Glycerol is one of the most critical raw materials in building polymer. In this study, glycerol is produced as a byproduct of the biodiesel manufacturing, while in some other polymer production operations, glycerol is obtained from crude oil due to its low price when obtained from that source ($0.20 /kg vs. $1.04 /kg) (Landress, 2017).

Fig. 4.9 compares the two scenarios for various glycerol sources. As observed in the figure, the unit production price from crude oil is $1.74 /kg, 28.98% lower than from vegetable oil. However, when considering the environmental impact of these two glycerol production

pathways, there is a 34.5% reduction in air emissions in the biodiesel production pathway compared to that of the petroleum production pathway (Sheehan et al., 1998). Even though the unit production cost is lower in the crude oil pathway, its influence on the environment is much larger.

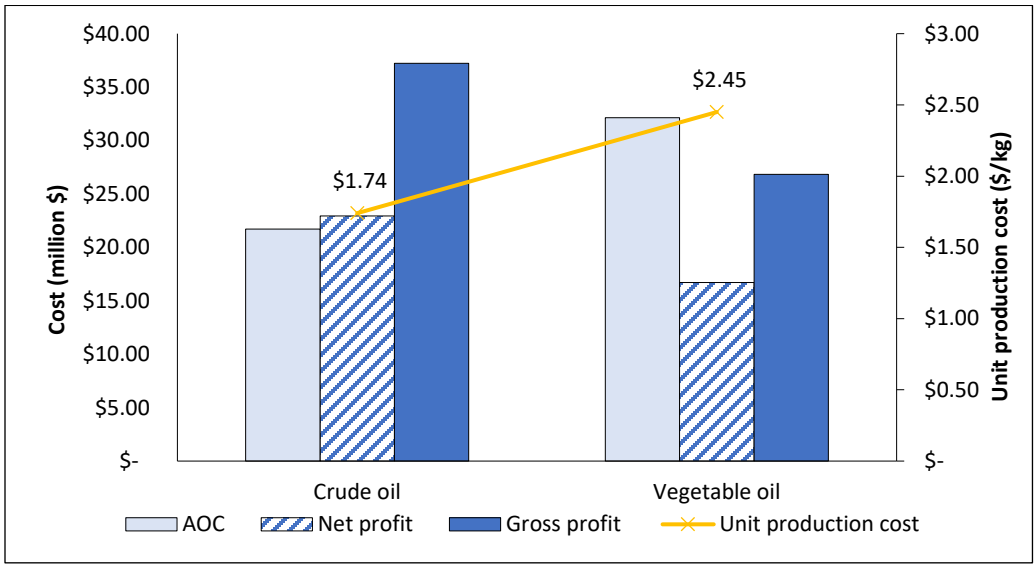


Figure 4.9 Scenario analysis results of glycerol sources for the structural bio-adhesive production process (AOC: annual operating cost).

Scenario analysis on bio-adhesive selling price

Prices for structural bio-adhesives vary widely, depending on application. In this study, the base-case scenario of the selling price of bio-adhesive based on the U.N. commodity data was chosen, resulting in a range of worst-case scenario and the best-case scenario within ±50%.

As shown in Fig. 4.10, in the worst-case scenario (-50%), both the gross profit and net profit are negative, indicating that no profit could be achieved when the market selling price is at $2.0 /kg or below, while in the best-case scenario (+50%), the gross profit and net profit doubled when compared with the base-case scenario. In addition, the payback time in the best-case scenario decreased from 3.5 years to 1.7 years.

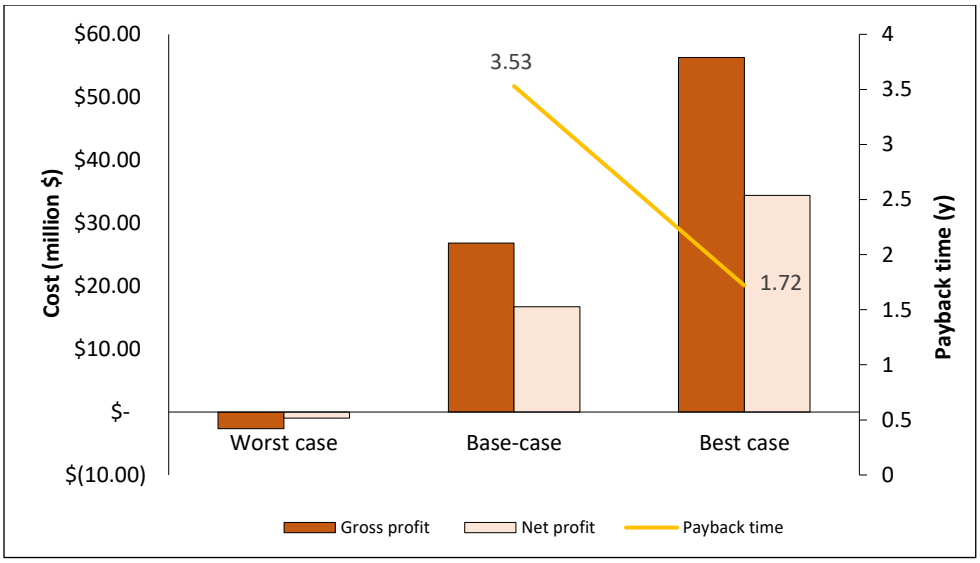


Figure 4.10 Scenario analysis results of selling price for the structural bio-adhesive production process.

Sensitivity analysis results

As illustrated in Fig. 4.11, the material cost is the most sensitive variable in terms of the unit production cost among all input variables. This implies that material cost drives the structural bio-adhesive production process developed in this study. By exploring the raw materials used in this research, it is found that the price of glycerol, acrylic acid, and catalyst are the most sensitive factors, and changes in any of these three materials will result in changes in the final product price (from $2.36 /kg to $2.53 /kg).

Capital cost is another important variable due to the uncertainty associated with the study. As discussed in previous scenario analysis, the changes of the total capital investment (C_{TCI}) has the second largest influence on the final product price, followed by working capital and startup cost. Except for material cost and capital cost, we found that labor cost is also quite critical in this study, suggesting that if administrative cost and supervisory cost are considered, the final product price may increase to $2.50 /kg.

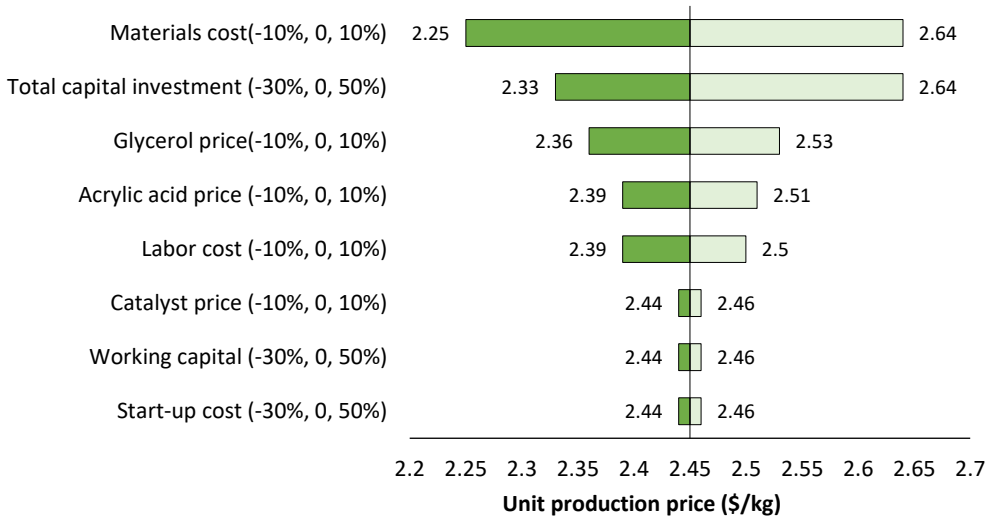


Figure 4.11 Sensitivity analysis of the structural bio-adhesive production process.

Discount cash flow (DCF) analysis

Fig. 4.12 depicts the cumulative discounted after-tax cash flow of the 40 t/d structural bio-adhesive production plant under various discount rates (i). If the time value of money is considered, the net present value (NPV) decreases from 187.7 million dollars to 46.8 million dollars at the end of the project (i = 10%). With a higher discount rate, the NPV decreased accordingly (NPV= 18.8 million dollars when i = 15%). The internal rate of return (IRR) is 17.87% as calculated, so this project is acceptable because IRR is larger than the discount rate (10% as assumed in *Methods*).

In addition, if NPV is zero and the price of the structural bio-adhesive is varied, the minimum selling price (MSP) is determined to be $3.11 /kg when the discount rate is 10%.

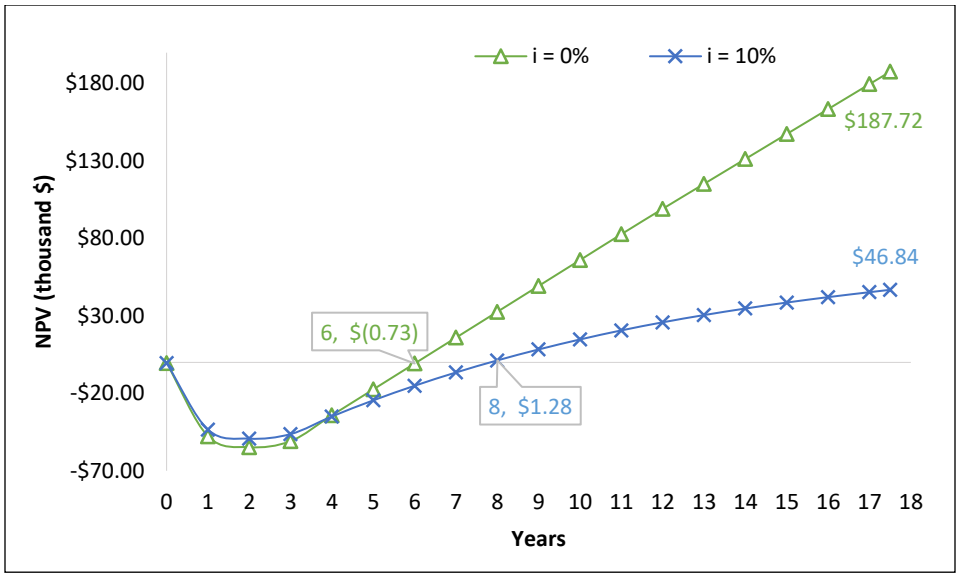


Figure 4.12 Cumulative discounted after-tax cash flow result of the structural bio-adhesive production process.

Conclusions

In this study, techno-economic analysis (TEA) was conducted to investigate the economic feasibility of a structural bio-adhesive production process. Five plant scales were explored using SuperPro Designer v9.5 software and, as expected, larger plant scale will increase the total capital investment and annual operating cost, even though the unit production cost will decrease at larger plant scale. The lowest unit production price obtained in this study is $2.45 /kg for a plant scale of 40 t/d.

Increasing uncertainty in the scenarios associated with the study will have some influence on unit production cost, but not on the net profit side. If crude-oil glycerol replaces biobased based glycerol, unit production price may reduce, but the associated environmental impact of the crude oil refinery process could significantly increase. We also found that the selling price of the structural bio-adhesive would have a large influence on economic factors.

Sensitivity analysis was carried to determine the most sensitive variable with respect to

product value, and this analysis indicated that the structural bio-adhesive production process is a material-driven process. Furthermore, exploration of cash flow based on calculation indicates that this project should be accepted because it can earn money, with the minimum selling price (MSP) of the structural bio-adhesive determined to be $3.11 /kg.

Given the uncertainty associated with the study, a more detailed future project analysis could be conducted to further explore the economic performance of this structural bio-adhesive production process.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

This study was funded by the National Institute of Food and Agriculture of the United States Department of Agricultural, under the project number 214-38202-22318.

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CHAPTER 5. ENVIRONMENTAL ASSESSMENT OF PRESSURE SENSITIVE BIOBASED ADHESIVE (PSA) PRODUCTION PROCESS MADE FROM GLYCEROL

Modified from a paper to be submitted to *Journal of Cleaner Production.*

Abstract

Environmental concerns over the petroleum-based adhesives have increased the research for more sustainable adhesives, especially in the wood production market. The purpose of this paper was to evaluate the potential environmental effect of glycerol-based pressure sensitive bio-adhesives (PSA) made from the reversible addition-fragmentation chain transfer (RAFT) polymerization process. GaBi 6 software was employed to perform the cradle to gate life cycle assessment (LCA), and TRACI was used as the life cycle impact assessment method. Several key parameters for life cycle analysis were analyzed, for instance: global warming potential (GWP), acidification potential (AP), eutrophication potential (EP), ozone depletion potential (ODP) and human health effects. The main result from this study showed that bio-adhesive has an environmental impact (3.84 kg CO_2-eq/kg bio-adhesive of global warming potential), which is lower than that of petro-adhesive. Sensitivity analysis was conducted in order to determine the key factors (electricity sources, transportation distance, and production yield) that influence the greenhouse gas emissions and energy consumption.

Keywords

Life cycle assessment (LCA); Glycerol; Pressure sensitive adhesive (PSA); RAFT polymerization; Sensitivity analysis.

Introduction

According to *Research and Markets*, the adhesive market worldwide is estimated to reach $53.50 billion by 2022 (Research and Markets, 2018). Adhesives have been used for a long history. However, until 20th century, large improvements were made in adhesive's production. Formaldehyde-based resin has been introduced to produce structural adhesive, which effectively raised the production amount of adhesive all over the world (Hartshorn, 1986).

One of the widely applied adhesives is named pressure sensitive adhesive (PSA). PSA can bond materials on their surface by applying pressure, and it has the ability to remain permanently tacky at room temperature (Doyle and O'Quinn, 2011). PSA has been applied in many areas, such as packaging tapes, automotive, electricity and medical industry (Mohammed et al., 2015). Based on the survey from *Stratistics Market Research Consulting (MRC)*, PSA market worldwide is anticipated to reach $13.63 billion by 2023 (Reuters, 2018).

Petrochemical, serves as the major material for adhesive production, is one of the largest products from petroleum refinery plant. According to the U.S. Environmental Protection Agency (U.S. EPA), 65% of the greenhouse gas (GHG) emissions come from carbon dioxide (EPA, 2018). Fossil fuel consumption is regarded as the primary sources of CO_2. Due to the increasing concerns of the environment and the non-renewable characteristics of fossil fuels, efforts have been made continuously to reduce the dependency of fossil fuel market.

Glycerol, a major raw material used in this study, is a quite versatile compound and great for the synthesis of a high number of organic chemicals, such as polymers (Tao et al., 2013). The production of glycerol has increased rapidly from the end of the 19th century because of increasing natural fats and oils (Behr et al., 2008). Today, a large amount of glycerol is generated as a co-product from biodiesel production plant. Main reaction happened during biodiesel production is shown in Fig. 5.1 below. Biodiesel market is quite promising since it increased

almost 20% in 2016 as compared with 2015 based on the U.S. Energy Information Administration (U.S. EIA)'s report (EIA, 2018).

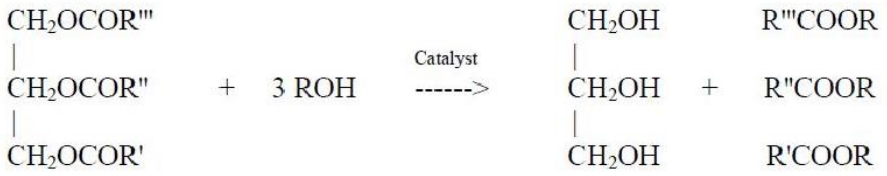

Figure 5.1 Chemical reaction of biodiesel.

In this study, the researchers in Iowa State University chose the reversible addition-fragmentation chain transfer (RAFT) polymerization process to conduct the polymerization experiment. Consequently, PSA is produced from the low molecular weight polymers made from the RAFT polymerization process. RAFT polymerization process was first reported by CSIRO in the late 1990s (Chiefari et al., 1998). RAFT polymerization process is regarded as the most convenient and flexible polymerization process because it can be applied to most vinyl monomers, and can be compatible under a variety of conditions (Moad et al., 2008). RAFT polymerization process is one of the most popular reversible deactivation radical polymerization (RDRP) techniques. An essential attribute of chain transfer is that the product of it is also a chain transfer agent with similar activity to the previous transfer agent (Moad et al., 2008). A chain transfer agent (CTA) or a RAFT agent is regarded as the key to a successful polymerization process.

Generally speaking, as shown in Fig. 5.2, RAFT polymerization process starts with an initiation step aimed at creating a propagating radical ($P_m^{\cdot}$). Then the radical is reversibly added to the chain transfer agent (CTA) to create a reinitiating group ($R^{\cdot}$). Following re-initiation, the main equilibrium RAFT polymerization process is dominant in growing the polymer chain until a termination reaction occurs.

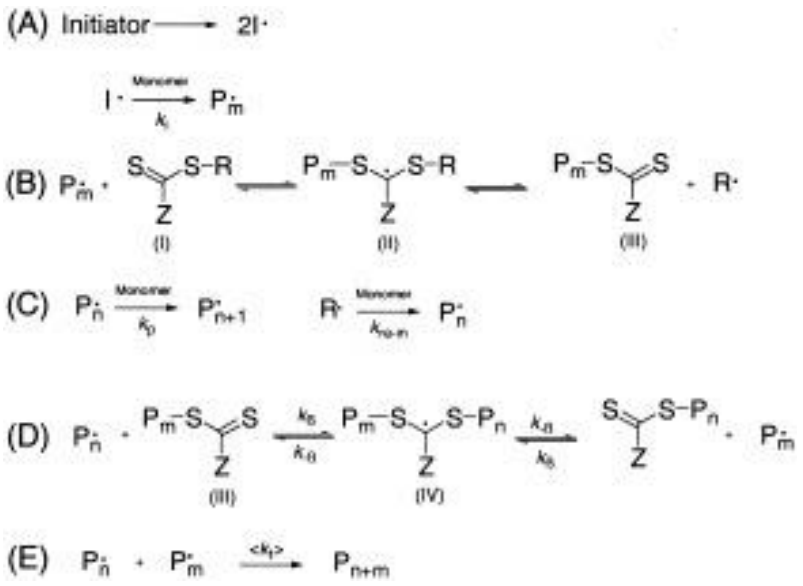

Figure 5.2 Mechanism of RAFT polymerization process (Hao et al., 2003).

The RAFT polymerization process can be carried out under environmental-friendly conditions, such as water-based solvent (Lowe and McCormic, 2007) and ionic liquids (Shakraborty et al., 2014). Moreover, RAFT polymerization process can be applied to renewable resources, and both organic and inorganic renewable materials can be polymerized via RAFT polymerization (Boyer et al., 2009). However, a number of renewables being used to manufacturing products are in low supply at present, mostly because economic value is the main driving factor of industry. Compared with petroleum goods, renewables are difficult to achieve a great economic benefit (Hernandez et al., 2014). In 2013, Cochran et al. broadened the RAFT polymerization application by creating novel thermoplastic homopolymer and block copolymers derived from plant oil or animal oil (Cochran et al., 2014). Based on their processes, PSA is further produced.

Environmental assessment of PSA is quantified from the life cycle assessment (LCA) method. LCA has been used to evaluate the environmental impact since 1970s. Early LCA primarily focused on standardization activities, for example, framework, terminology and basic

procedures. In late 1990s, the first international standards: ISO 14040: '*Environmental management – life cycle assessment – principles and framework*' has been introduced by the International Standard Organization (ISO, 1997). In 2006, a more detailed standards: ISO 14044: '*Environmental management – life cycle assessment – requirements and guidelines*' were developed by ISO (ISO, 2006). These two standards serve as the principles in current LCA studies.

There are four steps in a LCA study according to the two ISO standards (Fig. 5.3). First is to define goal and scope of the study, including objectives statement, selection of functional unit (FU) and the corresponding system boundary. Associated assumptions are also need to clarify in this phase. Then, life cycle inventory analysis is needed as phase two. In this step, the input and output within the system boundary is compiled and data is collected during this step. The third step is to conduct life cycle impact assessment. Proper impact assessment methods are chosen to categorize the environmental emissions and resource depletion. Results from impact assessment are converted to impact units to analyze environmental impacts. The last step is interpretation. This is the phase used to interpret the results from previous steps.

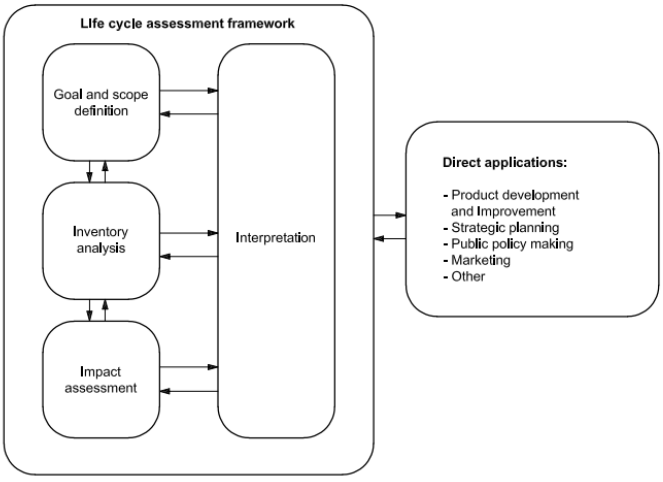

Figure 5.3 Stages of LCA study (ISO, 1997).

The main objective of this study is to evaluate the environmental impact of PSA production made from RAFT polymerization process. In order to fully understand the sustainability of this PSA production process, two glycerol production pathways were considered in this study: petro-glycerol scenario and bio-glycerol scenario.

Methods

Goal and scope definition

In this study, the LCA system boundary includes extraction of raw materials, monomer production and polymer production, aka cradle to gate. Fig. 5.4 exhibits the overall PSA production process from bio-glycerol (bio-glycerol scenario); Fig. 5.5 shows the PSA production process from petro-glycerol (petro-glycerol scenario). Comparisons of environmental impact are made between these two scenarios. The functional unit chosen for this study is 1 kg of PSA produced.

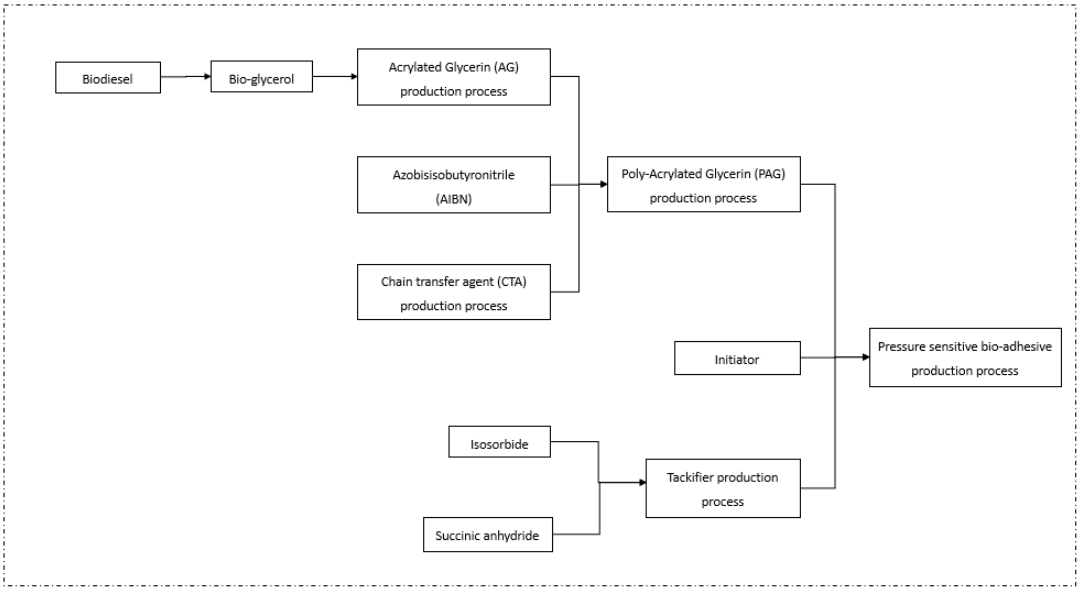

Figure 5.4 Simplified flowchart of PSA production process (bio-glycerol scenario).

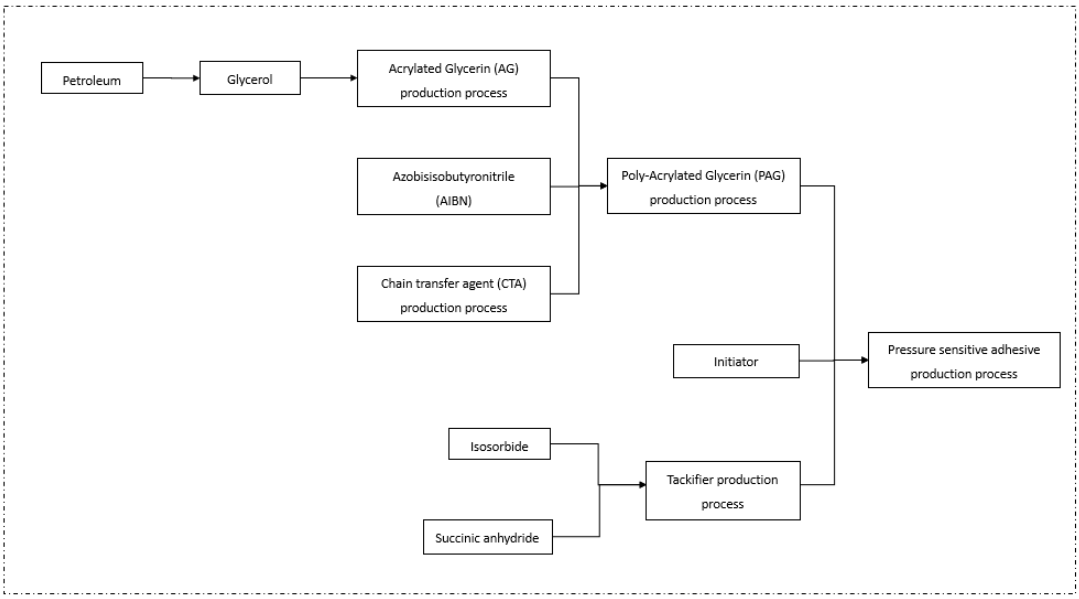

Figure 5.5 Simplified flowchart of PSA production process (petro-glycerol scenario).

Life cycle inventory

Data used in LCA modeling is mainly collected from Iowa State University's research laboratory results. Literatures, as well as reports and patents, was also used as background data. Databases, such as EcoInvent, GaBi, and U.S. life cycle inventory (U.S. LCI), were employed to cover data gaps.

The overall PSA production process is divided into five parts: 1) acrylated glycerol (AG) production process (Fig. 5.6); 2) chain transfer agent (CTA) production process (Fig. 5.7); 3) poly-acrylated glycerol (PAG) production process (Fig. 5.8); 4) tackifier production process (Fig. 5.9); 5) PSA production process (Fig. 5.10).

In bio-glycerol scenario, glycerol is obtained as a by-product from biodiesel production plant. Biodiesel plant data is collected from a U.S. Department of Energy biodiesel production report (Sheehan et al., 1998). The biodiesel production process started from soybean grain cultivation, soybean crushing to produce soybean oil, and oil transesterification process to

produce biodiesel. Crude glycerol of 80% wt. is obtained as a co-product from biodiesel plant. As reported by Sheehan et al., the mass ratio between crude glycerol and biodiesel is about 150 to 1,000 (0.15 to 1). The material inputs include soybean oil, methanol, and water; Catalysts such as sodium hydroxide are added as well. In terms of energy inputs, it is reported that when producing 1,000 kg of biodiesel, 28.9 kWh electricity and 1,356 Mt of steam are required (Sheehan et al., 1998). As for petro-glycerol scenario, glycerol is produced from petroleum refinery plant. GaBi database is use in modeling this process. After glycerol is produced from either biodiesel plant or petroleum refinery plant, acrylic acid along with catalysts (amberlyst and phenothiazine) are added to produce acrylated glycerol. The temperature required in AG production process is around 100°C for 5 hours.

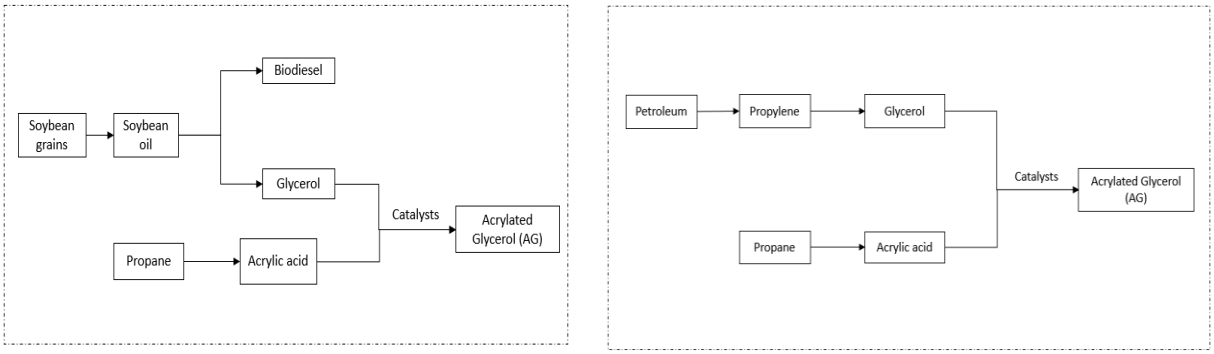

Figure 5.6 Acrylated glycerol (AG) production process (Left: bio-glycerol scenario; Right: petro-glycerol scenario).

Chain transfer agent (CTA) is a critical component in RAFT polymerization. Its production process is depicted in Fig. 5.7. Ethanethiol is first added with potassium hydroxide for around 30 minutes for neutralization purpose; after that, carbon disulfide is added to react with the neutralized solution; About 30 minutes later, 3-chloro-2-butanone is added to produce

CTA. Acetone is act as a buffer solution in CTA production, and the recycle rate is set at 97% as suggested by professional polymer researchers. The whole CTA production process is conducted under mild temperature and pressure.

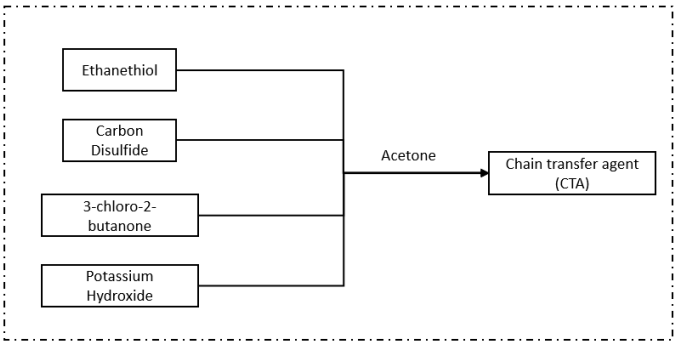

Figure 5.7 Chain transfer agent (CTA) production process.

Once AG and CTA are produced, the second part of RAFT polymerization can be proceed with azobisisobutyronitrile (AIBN) acts as catalyst. Poly-acrylated glycerol (PAG) with low molecular weight (10,000 g/mole) is produced afterwards. This process is estimated to take 2 hours at 70°C.

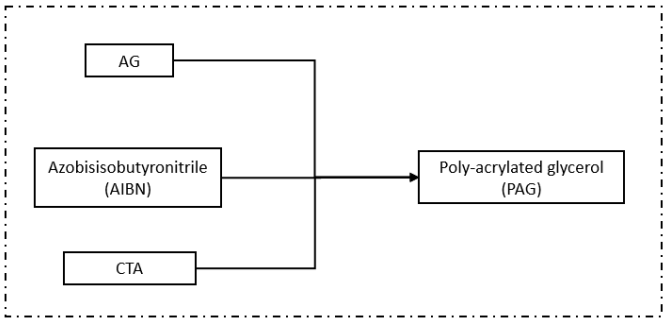

Figure 5.8 Poly-acrylated glycerol (PAG) production process.

Tackifier is produced from Isosorbide and succinic anhydride with molar ratio of 1 to 2.2. This production process takes place at 80°C for approximately 2 hours. The last procedure is to produce PSA from PAG, tackifier and initiator as shown in Fig. 5.9.

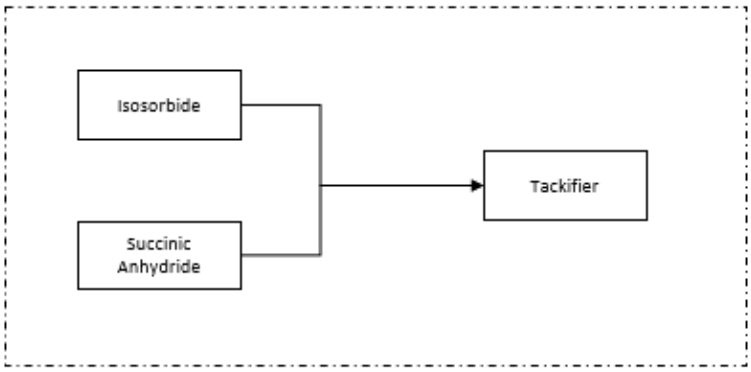

Figure 5.9 Tackifier production process.

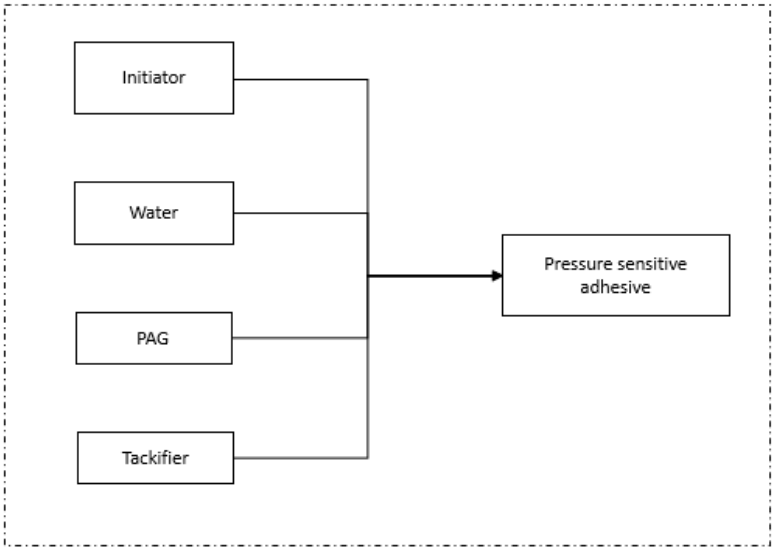

Figure 5.10 PSA production process.

Electricity data is collected from the U.S. Energy Information Administration (U.S. EIA) (EIA, 2006). As shown in Table 5.1, approximately 60% of electricity in Iowa is produced from fossil fuel, followed by 14% from wind energy. This electricity data is used in life cycle impact assessment calculation.

Table 5.1 Electricity sources in Iowa, 2016.

Energy source	Percentage
Fossil fuels	57.83%
Hydroelectric	17.81%
Wind	13.82%
Nuclear	3.65%
Wood and wood-derived fuel	2.41%
Solar Photovoltaic	1.95%
Geothermal	1.01%
Landfill gas	0.67%
Biogenic municipal waste	0.44%

Life cycle impact assessment

In this study, two life cycle impact assessment methods were chosen. One is the U.S. EPA's Tool for the Reduction and Assessment of Chemicals and Other Environmental Impacts (TRACI 2.1); and the other is Eco-Indicator 99 (EI 99). The difference between these two methods is that TRACI is a mid-point impact assessment approach, while EI 99 is an end-point assessment approach.

The impact categories in TRACI 2.1 include global warming potential (GWP), acidification potential (AP), eutrophication potential (EP), ozone depletion potential (ODP), human health impacts, smog formation and ecotoxicity (EPA, 2018). As for EI 99, three damage categories (human health, ecosystem quality and resources) are contained. The results from EI 99 is expressed in one single score of the overall environmental impacts (Dreyer et al., 2003).

Table 5.2 Damage categories in Eco-indicator 99.

Damage categories	Impact categories
Human health	Climate change
	Ozone layer depletion
	Carcinogenic effects
	Respiratory effects
	Radiation
Ecosystem quality	Ecotoxicity
	Acidification
	Eutrophication
	Land use
Resources	Fossil fuels
	Minerals

Sensitivity analysis

Sensitivity analysis for climate change, represented by global warming potential (GWP), was carried out in order to determine the most sensitive factor throughout PSA's entire life cycle. In this study, transportation distance, electricity sources, and production yield were chosen to conduct the sensitivity analysis.

Results and Discussion

LCA results

As shown in Table 5.3, when producing 1 kg of PSA, 3.84 kg CO_2-eq of global warming air is emitted from bio-glycerol scenario and 6.12 kg from petro-glycerol scenario. Acidification potential of both scenario is similar (1.26 kg H+ moles-eq. in bio-glycerol scenario vs. 1.34 kg H+ moles-eq. in petro-glycerol scenario). However, when looking at ozone depletion air, we

notice that nearly three-fold more emission is produced in petro-glycerol scenario. This is largely resulted from the petroleum refinery process. In term of the cancer air and particulate air, petro-glycerol scenario has higher impact as well.

Table 5.3 TRACI results of bio-glycerol scenario and petro-glycerol scenario.

Impact method	**Bio-glycerol Scenario**	**Petro-glycerol Scenario**
TRACI global warming [kg CO_2-eq/FU]	3.84	6.12
TRACI acidification [kg H+ moles-eq/FU]	1.26	1.34
TRACI eutrophication [kg N-eq/FU]	1.42E-03	1.11E-03
TRACI ozone depletion air [kg CFC 11-eq/FU]	2.03E-11	8.91E-11
TRACI smog air [kg O_3-eq/FU]	0.22	0.27
TRACI human health particulate air [kg PM 2.5-eq/FU]	1.18E-03	1.36E-03
TRACI human health, cancer air [CTUh/FU]	1.05E-09	1.14E-09

As for the overall environmental impact, petro-glycerol scenario has a higher environmental impact score (3.8 pts) than bio-glycerol scenario (2.2 pts) with a difference of nearly 40% (Fig. 5.11). Not surprisingly, other work in this field has similar results. In 2014, McDevitt and Grigsby did a comparison of bio-adhesives and petro-adhesives used in fiberboard production in New Zealand; they found that the overall environmental impact of biobased materials has a 22% lower EI 99 result than petrochemicals (McDevitt and Grigsby, 2014). Our previous exploration on environmental impacts of structural adhesive showed that petro-glycerol scenario may result in almost 30% higher environmental impact than bio-glycerol scenario.

It is found that resource depletion in petro-glycerol scenario is much higher than bio-glycerol scenario (2.0 pts vs. 0.9 pts). As for human health impact and ecosystem quality impact, petro-glycerol scenario is slightly higher (less than 5%) than bio-glycerol scenario.

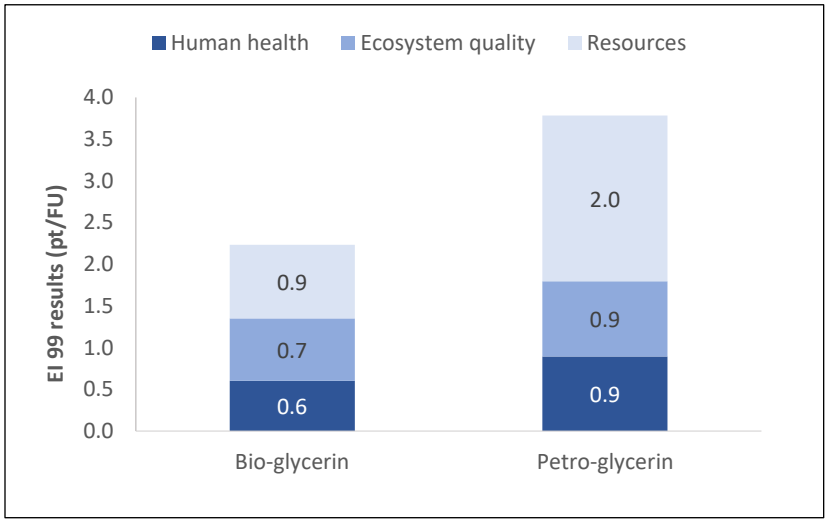

Figure 5.11 Eco-Indicator 99 results of two scenarios in PSA production process.

Energy consumption

Fig. 5.12 shows the energy consumption of these two scenarios. It is observed that petro-glycerol scenario requires more energy than that in bio-glycerol scenario (116 MJ/FU vs. 84.8 MJ/FU). In bio-glycerol scenario, nearly 40% of the energy is used in glycerol production; while in petro-glycerol scenario, 55% of the energy is needed in glycerol production. In other words, when comparing the two pathways of glycerol production, petroleum refinery process needs more energy than biodiesel production process.

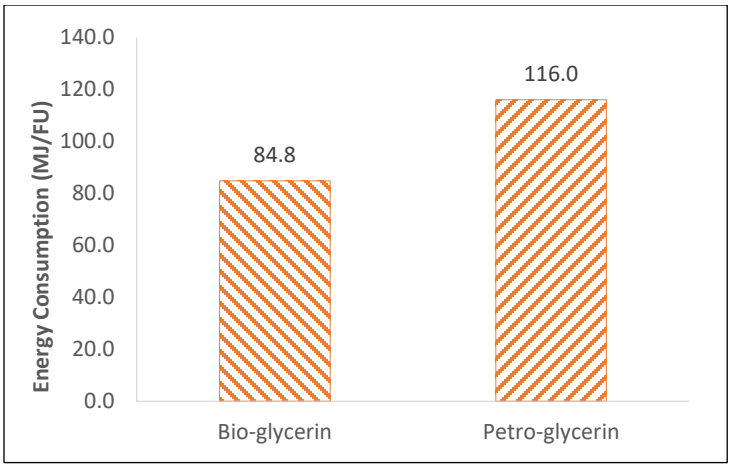

Figure 5.12 Energy consumption of two scenarios in PSA production process.

Sensitivity analysis

Sensitivity analysis has been conducted to determine the most sensitive parameter in the PSA production process. Some input factors, such as electricity sources, production yield and transportation distance, are used in sensitivity test in terms of greenhouse gas (GHG) emissions (expressed as global warming potential).

The first parameter is the electricity sources. As mentioned in previous, nearly 60% of the electricity sources in Iowa was fossil fuels. The GHG emission in this scenario was estimated to be 3.84 kg CO_2-eq/MJ of electricity. When we replace the electricity to 100% renewable sources, like biomass, the GHG emission reduces to 2.12 kg CO_2-eq/MJ of electricity. On the other hand, if 100% coal is used to generate electricity, 5.31 kg CO_2-eq/MJ GHG emission is produced; compared to current scenario, the increase is nearly 35%. The result of the sensitivity analysis on electricity sources (Fig. 5.13) indicates that by replacing the energy sources to renewable sources, the environmental impact could be largely decreased.

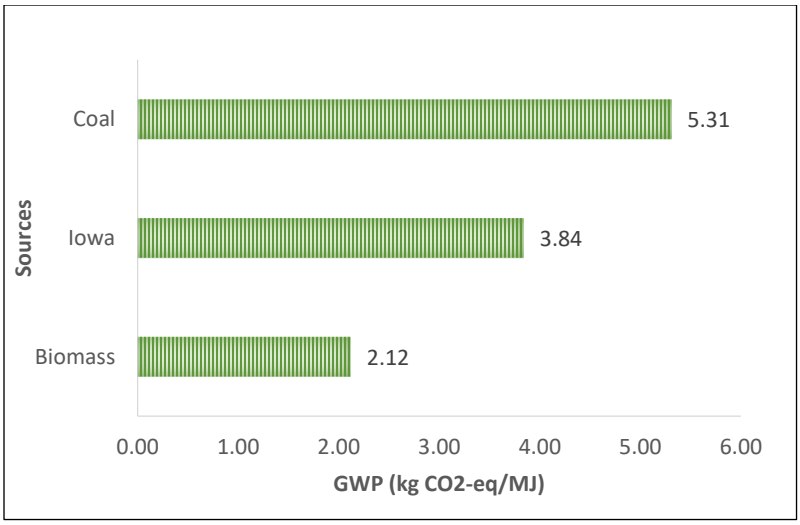

Figure 5.13 Sensitivity analysis of PSA on electricity sources.

The second sensitivity test is on production yield. In this study, based on the laboratory results, the final production yield is assumed 100%. If scaling up, production yield may vary. Therefore, we investigated the GHG emission under different production yield. As shown in Fig. 5.14, when production yield decreases by 5%, the GHG emission increases to 4.02 kg CO_2-eq/FU (about 5% higher); if continue decreasing to 90%, 4.25 kg CO_2-eq/FU GHG emission is observed.

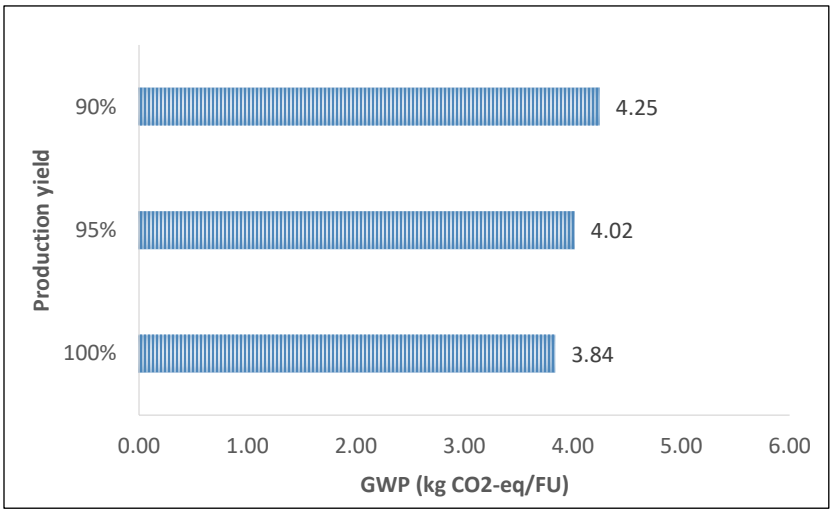

Figure 5.14 Sensitivity analysis of PSA on production yield.

The third parameter we test is the transportation distance. In this study, we explored the GHG emissions within the range of 1,000 miles (Fig. 5.15). However, the GHG emissions increase slightly (from 3.84 kg CO_2-eq/FU to 3.89 kg CO_2-eq/FU); and the associated energy consumption only increases 1MJ/FU. This indicates that the transportation distance is not as sensitive as electricity sources in terms of GHG emission.

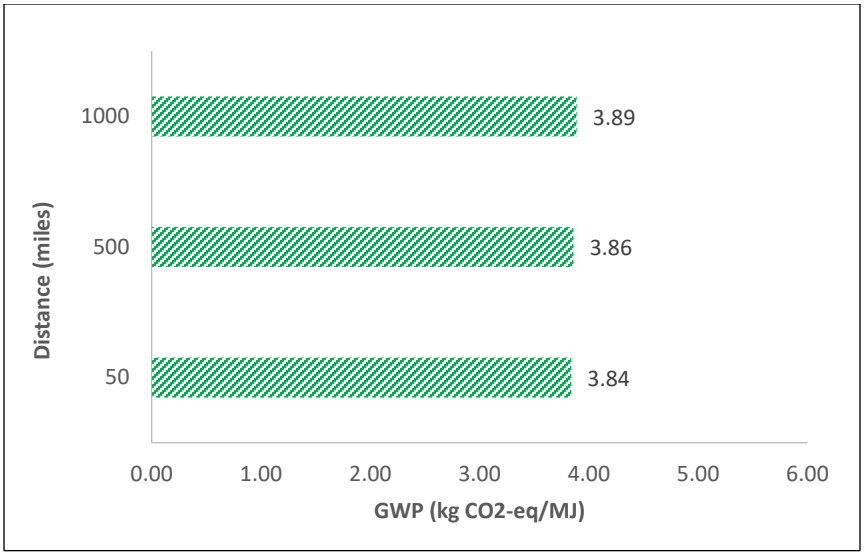

Figure 5.15 Sensitivity analysis of PSA on transportation distance.

Conclusion

In this study, a life cycle assessment (LCA) study was conducted to quantify the environmental impact of the pressure sensitive adhesive (PSA) made from reversible addition-fragmentation chain transfer (RAFT) polymerization process. The results showed that by producing 1 kg of PSA, the global warming potential (GWP) is estimated to be 3.84 kg CO_2-eq. As for the energy consumption, 84.8 MJ is required in order to produce 1 kg PSA. Compared with petro-glycerol scenario, PSA produced from bio-glycerol scenario has less environmental impact (40% lower in bio-glycerol scenario). The results from sensitivity analysis suggest that

electricity sources have large impact on the final greenhouse gas emission, followed by production yield. In terms of transportation distance, it is not as significant as the previous factors. Because of the uncertainty associated with input parameters and model itself, future study could be conducted to further explore environmental impact of PSA process, such as social environmental impact.

Acknowledgements

This study was funded by the National Institute of Food and Agriculture of the United States Department of Agricultural, under the project number 214-38202-22318.

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CHAPTER 6. A TECHNO-ECONOMIC ANALYSIS STUDY OF THE PRESSURE SENSITIVE BIOBASED ADHESIVE PRODUCTION MADE FROM REVERSIBLE ADDITION-FRAGMENTATION CHAIN TRANSFER (RAFT) POLYMERIZATION PROCESS

Modified from a paper to be submitted to *Journal of Cleaner Production.*

Abstract

With increasing environmental concerns with respect to the petroleum-based adhesives production process, bio-based adhesives have been explored as a promising replacement. The purpose of this paper was to explore the economic feasibility of pressure sensitive bio-adhesives made as glycerol, a byproduct of biodiesel production. SuperPro Designer v9.5 software was employed to perform the techno-economic analysis (TEA). Several key parameters were analyzed, such as total capital investment, annual operating costs and revenues. It was found that the unit production price of pressure sensitive bio-adhesives in the current market ($2.76 /kg) was compatible with that of pressure sensitive adhesives in general. Sensitivity analysis was also performed to evaluate the key parameters significantly influencing the economic results. In this study, material cost was determined to be the most significant factor throughout the production process. Discounted cash flow analysis (DCF) was conducted to explore the influence of the time value of money. The minimum selling price (MSP) was obtained for net present value (NPV) = 0 was $3.48 /kg for this bio-adhesive production process.

Keywords

Techno-economic analysis (TEA); Glycerol; Pressure sensitive adhesives (PSA); RAFT polymerization.

Introduction

According to the U.S. Environmental Protection Agency (U.S. EPA), 65% of the global greenhouse gas (GHG) emission come from carbon dioxide (CO_2); among which, fossil fuel consumption is the primary source of CO_2 (U.S. EPA, 2018). However, since oil refinery processing could provide varieties of raw materials for industrial manufacturing products, such as asphalt, diesel, fuel oil, petrochemicals and so on, fossil fuel serves as the root of the current global economy. As reported by the U.S. Energy Information Administration (U.S. EIA), crude oil production in U.S. raised to 9.41 million barrels per day in 2015; in 2016, there was a slight decrease (8.86 million barrels per day) in U.S. field (U.S. EIA, 2018). Still, the overall trend as shown in Fig. 6.1 implies the growing market of crude oil products. Because of the increasing concerns of the environment and the non-renewable and exhaustible characteristics of fossil fuels, numerous efforts have been made in order to reduce the dependency of fossil fuel market.

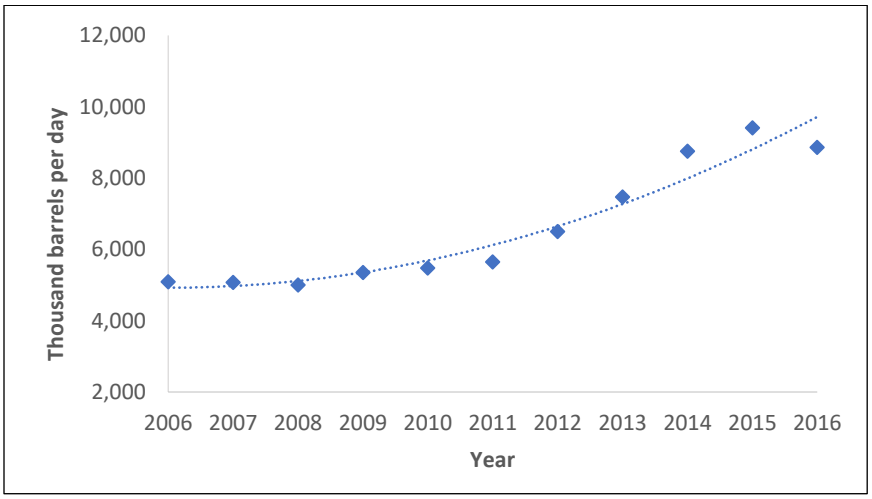


Figure 6.1 Crude oil production in U.S. from 2006 to 2016 (U.S. EIA, 2018).

Petrochemical is one of the largest products from crude oil processing. Typically, two common petrochemical types are olefins and aromatics, which are regarded as building blocks for a wide range of materials, for example, solvent and adhesive (Matar and Hatch, 2001).

Worldwide adhesive market will reach US$ 53,503.0 million by 2022 as estimated by *Research and Markets* (Research and Markets, 2018). Environmental-friendly and green sustainable adhesives offer significant opportunities for growing adhesive markets.

There are various means to categorize adhesive. On the form of cross-linked molecules, it can be divided into thermosetting or thermoplastic adhesive; based on chemical families, it can be classified by epoxy, polyurethanes, and polyimides; with respect to its functional types, it can be categorized by structural adhesive, hot met adhesive, pressure sensitive adhesive and so on. In this study, pressure sensitive adhesive is used as the target product.

A pressure sensitive adhesive (PSA) is the kind of adhesive used to bond materials mainly on their surfaces by applying pressure. The unique characteristic of PSA is that it has the ability to remain permanently tacky at room temperature (Doyle and O'Quinn, 2011). PSAs are widely applied polymeric materials in packaging tapes, self-adhesive labels, automotive, electric and medical industry (Mohammed et al., 2015). The demand in PSA has increased rapidly over the last decades. According to *Stratistics Market Research Consulting (MRC),* global PSA market is expected to reach $13.63 billion by 2023 (Reuters, 2018).

Major materials used in PSA formulation include natural rubber, styrene-butadiene-styrene (SBS), poly-isobutylene (PIB), nitrile rubber (NBR) and poly-acrylates (Sun et al., 2013). Poly-acrylates are broadly adopted because of the good stability over various temperatures and more resistance to external factors (Tape, 2018). Poly-acrylates can be produced by several processes, emulsion polymerization is selected as the most important one in industry (Penzel, 2000).

In this study, researchers chose the reversible addition-fragmentation chain transfer (RAFT) polymerization process to conduct the polymerization experiment. RAFT

polymerization process was first reported by CSIRO in the late 1990s (Chiefari et al., 1998). RAFT is regarded as the most convenient and flexible polymerization process because it can be applied to most vinyl monomers, and can be compatible under a variety of conditions (Moad et al., 2008). RAFT polymerization process is one of the most popular reversible deactivation radical polymerization (RDRP) techniques. An essential attribute of chain transfer is that the product of it is also a chain transfer agent with similar activity to the previous transfer agent (Moad et al., 2008). A chain transfer agent (CTA) or a RAFT agent is regarded as the key to a successful polymerization.

In general, the RAFT polymerization process begins with an initiation step to create a propagating radical ($P_m^{\cdot}$) (Fig. 6.2). After that, the radical is reversibly added to the chain transfer agent (CTA) to create a reinitiating group ($R^{\cdot}$). Following re-initiation, the main equilibrium RAFT polymerization process is dominant in growing the polymer chain until a termination reaction occurs.

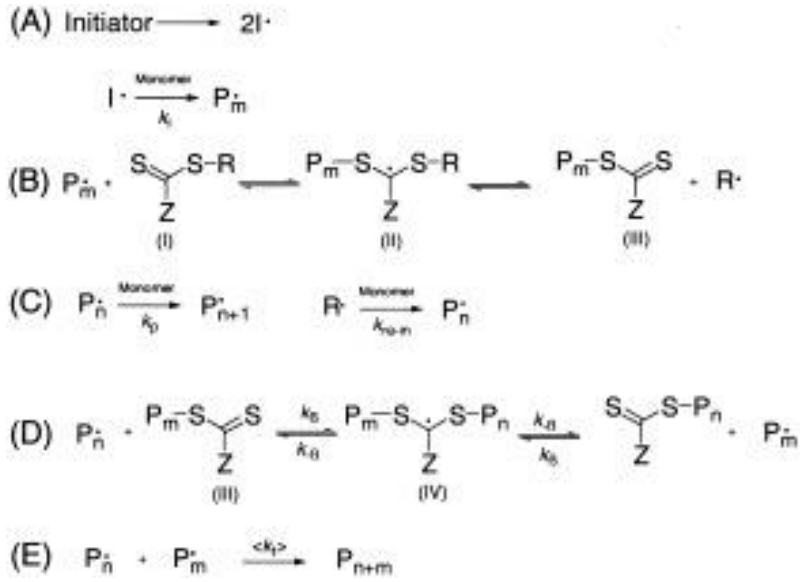


Figure 6.2 Mechanism of RAFT polymerization process (Hao et al., 2003).

One advantage of the RAFT polymerization process is that it can be carried out under environmental-friendly conditions like water-based solvent (Lowe and McCormic, 2007) and ionic liquids (Shakraborty et al., 2014). In addition, the RAFT polymerization process can be applied to renewable resources, and both organic and inorganic renewable materials can be polymerized via RAFT polymerization (Boyer et al., 2009). However, due to less economic values from renewables, less renewables are being used to manufacturing products compared with petroleum goods (Hernandez et al., 2014). In 2013, Cochran et al. broadened the RAFT polymerization application by creating novel thermoplastic homopolymer and block copolymers derived from plant oil or animal oil (U. S. Patent US 2014/0343192 A1, 2014).

Techno-economic analysis (TEA) is a process-modeling approach for simulating the production process as a whole. TEA includes both technical parameters and economic factors in project analysis (Chau et al., 2009). TEA starts with material and energy balance, and cost configuration is then conducted to assess a product's economic feasibility. The literature on TEA is extensively explored in the area of renewable energy, and in the realm of biochemical production, TEA is substantially used for evaluating economic feasibility of a production process.

In this study, a techno-economic analysis study was carried out to explore the profitability of pressure sensitive biobased adhesive (PSA) production made from reversible addition-fragmentation chain transfer (RAFT) polymerization process. The primary objectives of this study were to model the PSA production process and to evaluate the economic feasibility of this process. Sensitivity analysis was conducted to determine the crucial parameters on the product value ($/kg). Cash flow analysis was employed to explore the minimum selling price (MSP).

Methodology

The production process of the PSA was modeled in five scales: 1 t/d, 2 t/d, 5 t/d, 10 t/d, and 40 t/d. The largest scale (40 t/d) was chosen based on a real industrial resin production plant shown in Phoenix Equipment Corporation (Phoenix Equipment Corporation, 2016). Mass balance was performed in SuperPro Designer v9.5 software *(*Intelligen Inc., Cambridge, Massachusetts, USA). Major data used in modeling was collected from Iowa State University (ISU) laboratory results.

Process design

Fig. 6.3 shows a simplified flowchart of the overall PSA process. The thorough process model was built in SuperPro Designer. Several areas were included in this process: acrylated glycerin (AG) production, chain transfer agent (CTA) production, poly-acrylates (PAG) production, tackifier production, and PSA production.

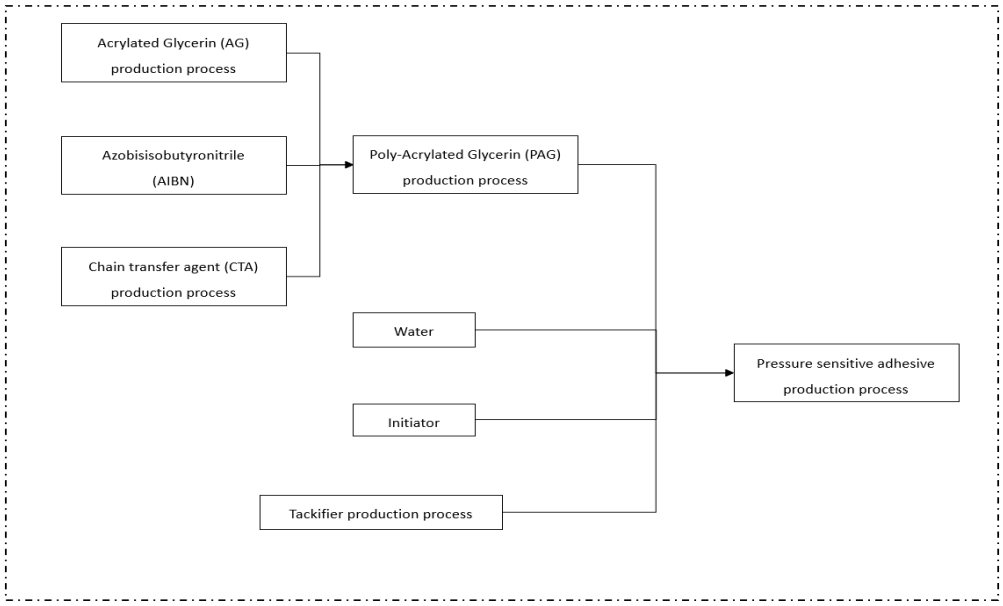


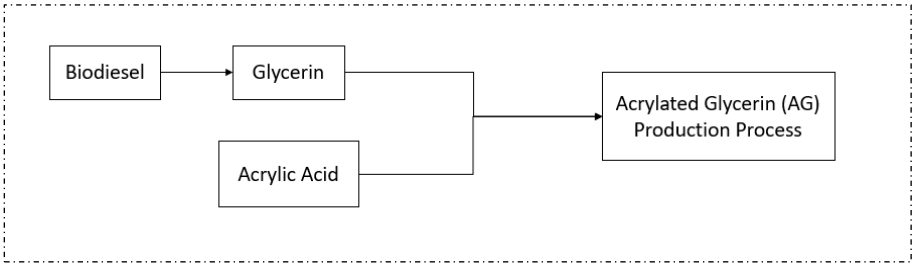
Figure 6.3 Simplified overall flowchart of the PSA production process.

This PSA production process begins with acrylic acid and bio-based glycerin from the biodiesel industry. Acrylated glycerin (AG) is produced through Fisher esterification of these two materials, as shown in Fig. 6.4 (A), with Amberlyst-15 and phenothiazine (PTZ) adopted as catalysts during esterification. This process is conducted under mild temperature and atmospheric conditions.

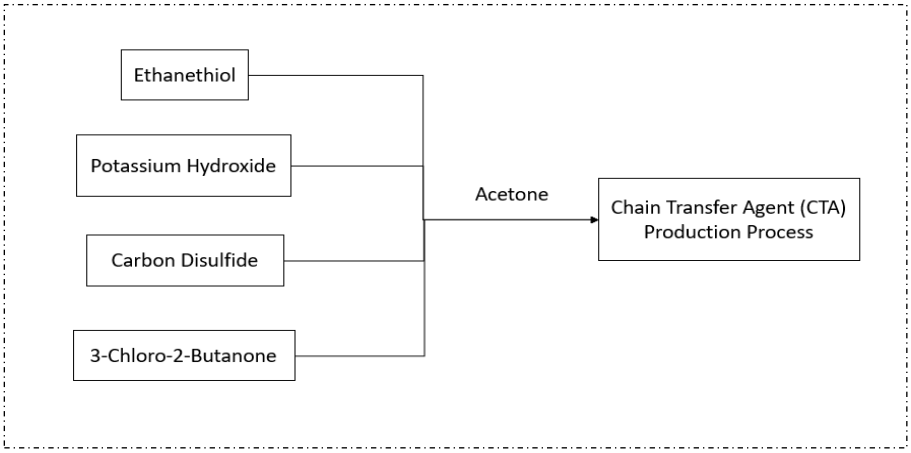
After the AG is produced, the RAFT polymerization process begins as a two-step process with the initial process one of producing AG monomer. The second step is to produce polymerized acrylated glycerin (PAG). As previously discussed, the RAFT agent or the chain transfer agent (CTA) is the most important component in the polymerization process. Fig. 6.4 (B) shows the materials used to produce the CTA. Ethanethiol is neutralized with KOH for 30 minutes, then CS_2 is reacted with a pH neutral solution for 30 minutes, 3-chloro-2-butanone is added afterward, and the mixture allowed to stir for 30 minutes. Acetone is used as the buffer solution during the CTA production, and is recycled for continuous production with a recycle rate of 97%. Potassium chloride (KCl) is produced as a byproduct of this process. The CTA is purified through the distillation column, and after purification, the CTA is reacted with AG and Azobisisobutyronitrile (AIBN) to perform RAFT polymerization. The reaction proceeds at 70°C for 2 hours. At the end of the RAFT polymerization, water is added to precipitate the polymer.

Tackifier is produced from isosorbide and succinic anhydride with the molar ratio of 1 to 2. After polymerization process, an initiator (4, 4’-azobis) is added to produce PSA.

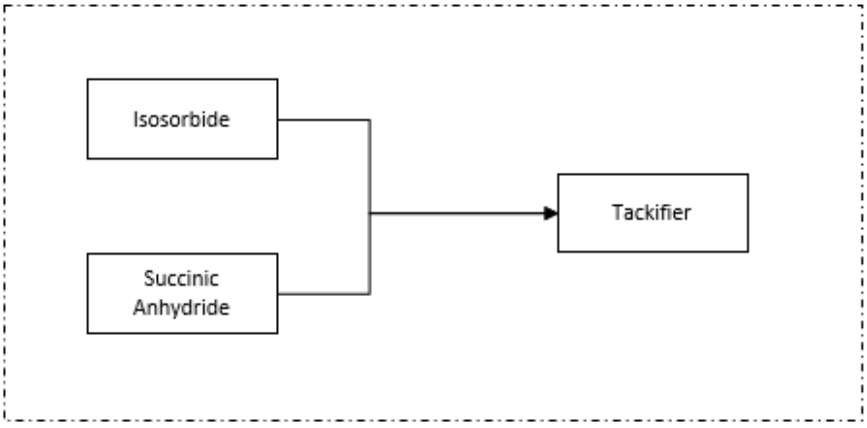
Computer models generated from SuperPro Designer are shown in Fig. 6.5, Fig. 6.6, and Fig. 6.7.



(A)



(B)



(C)

Figure 6.4 A detailed flowchart for (A) acrylated glycerin (AG) production process, (B) chain transfer agent (CTA) and (C) tackifier production process.

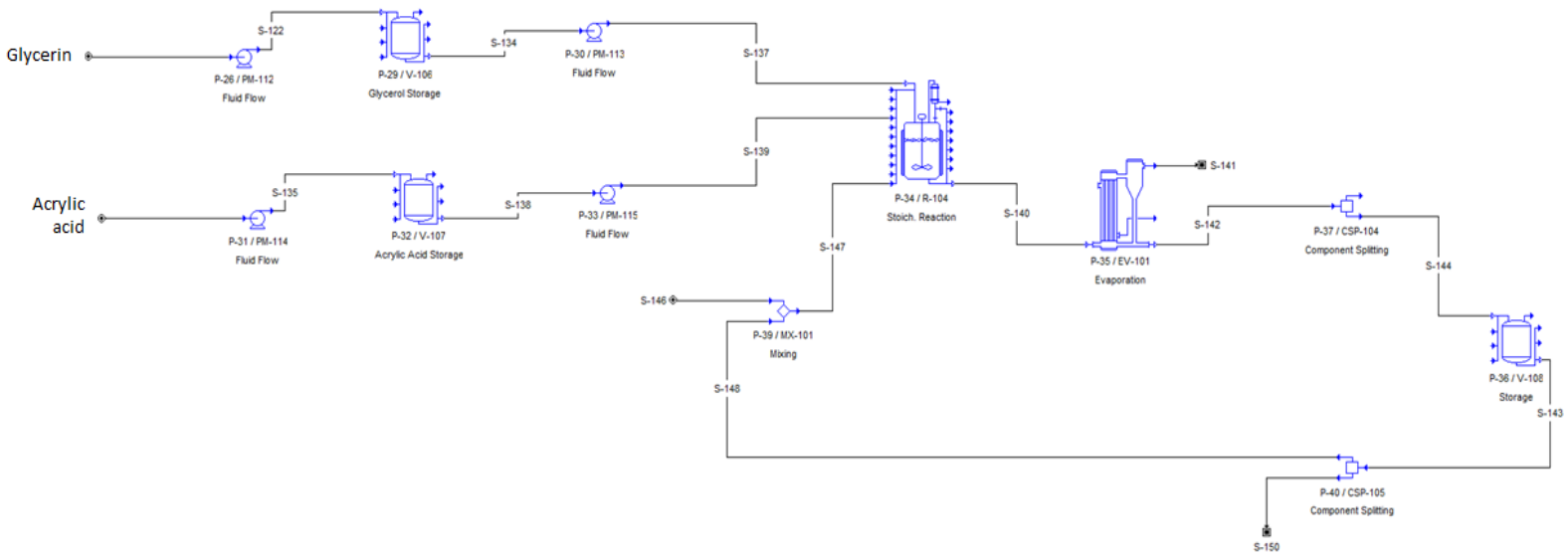


Figure 6.5 Computer model built in SuperPro Designer software (AG production process).

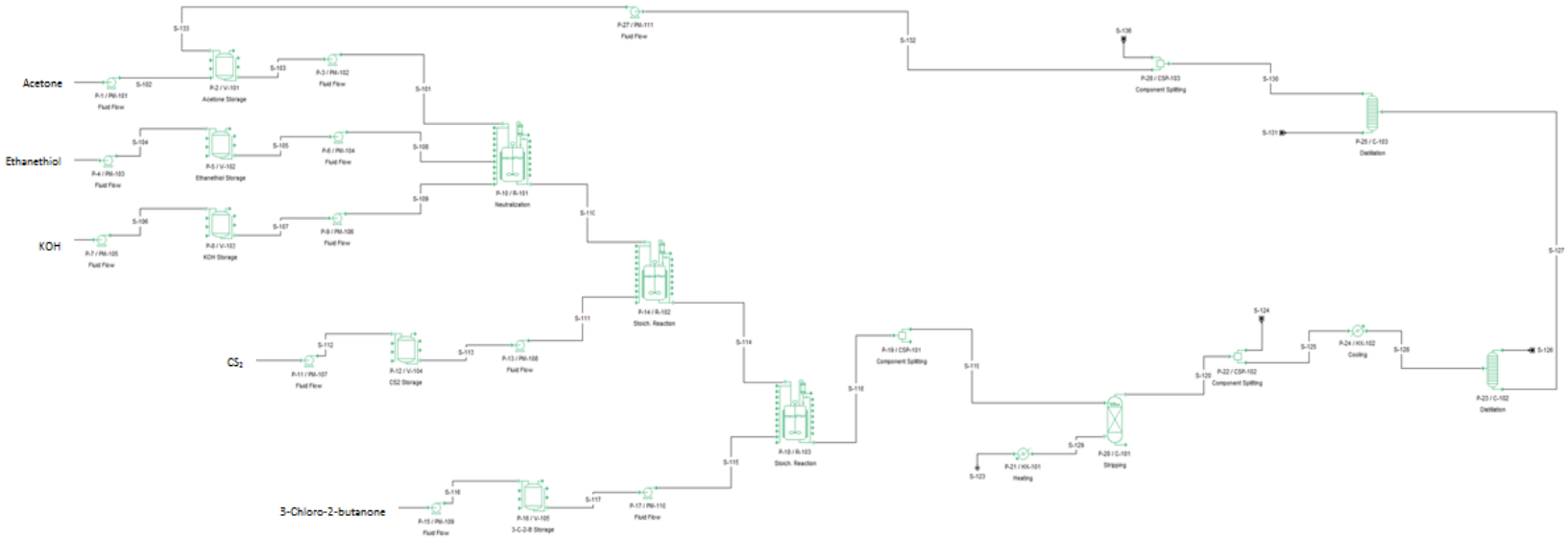


Figure 6.6 Computer model built in SuperPro Designer software (CTA production process).

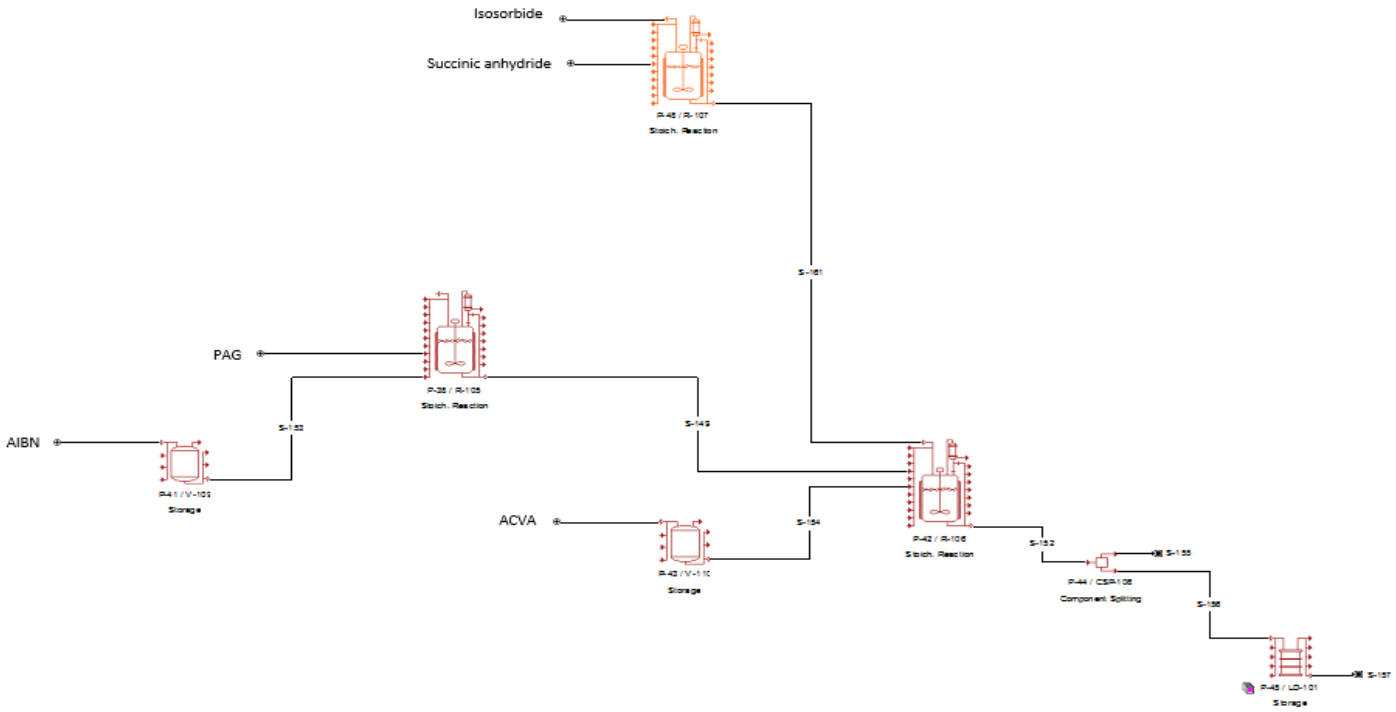


Figure 6.7 Computer model built in SuperPro Designer software (RAFT Polymerization, tackifier and PSA production process).

Economic analysis

The economic performance was explored by estimating the total capital cost (C_{TCI}), annual operation cost (C_{AOC}), and revenues.

Total capital cost (C_{TCI}) analysis

The total capital cost was calculated by sum of direct fixed capital cost (C_{DFC}), working capital (C_W), and startup cost (C_S) (Eq. 6.1). Working capital is the money invested in getting a plant into productive operation (Ulrich, 1984); Start-up costs are the costs to make the transition from construction to operation (Humphreys, 2005). It is assumed that this PSA production plant is located in central Iowa. The assumed construction time is 24 months, and the assumed start-up time is 6 months. The online time is assumed to be 329 days per year (7,896 h/y), equivalent to a capacity factor of 90% and assumed plant life is 15 years. The assumptions for total capital cost investment (C_{TCI}) are listed in Table 6.1. SuperPro Designer v9.5 software is employed to estimate the equipment purchase costs, and other assumptions were obtained from Peters et al. (Peters et al., 2015).

$$C_{TCI} = C_{DFC} + C_W + C_S \quad \text{(Eq. 6.1)}$$

Table 6.1 Assumptions used to model the total capital cost investment (C_{TCI}).

Parameters	Assumptions	Sources
1. Direct fixed capital cost (C_{DFC})	$C_{DC} + C_{IC} + C_{OC}$	
1) Direct cost (C_{DC})		
Equipment purchase cost (C_{PC})		SuperPro Designer database
Piping	0.68* C_{PC}	Peter et al., 2015
Instrumentation	0.50* C_{PC}	Peter et al., 2015
Insulation	0.03* C_{PC}	Peter et al., 2015

Table 6.1. (continued)

Parameters	Assumptions	Sources
Electrical facilities	0.30* C_{PC}	Peter et al., 2015
Building	0.45* C_{PC}	Peter et al., 2015
Yard improvement	0.20* C_{PC}	Peter et al., 2015
Auxiliary facilities	0.55* C_{PC}	Peter et al., 2015
Installation	0.55* C_{PC}	Peter et al., 2015
Land	0.08* C_{PC}	Peter et al., 2015
2) Indirect cost (C_{IC})		
Engineering	0.30* C_{DC}	Heinzle et al., 2006
Construction	0.35* C_{DC}	Heinzle et al., 2006
3) Other cost (C_{OC})		
Contractor's fee	0.06*(C_{DC} + C_{IC})	Peter et al., 2015
Contingency	0.08*(C_{DC} + C_{IC})	Peter et al., 2015
2. Working capital (C_W)	0.15* C_{DFC}	Ulrich, 1984
3. Start-up and validation cost (C_S)	0.10* C_{DFC}	Peter et al., 2015

Annual operating cost (C_{AOC}) analysis

Annual operating cost includes material cost (C_M), utility cost (C_U), labor cost (C_L), and facilities cost (C_F) (Eq. 6.2). Economic assumptions are listed in Table 6.2.

$$C_{AOC} = C_M + C_U + C_L + C_F \quad \text{(Eq. 6.2)}$$

Material costs are obtained from retailer websites, as detailed in sources. The electricity price is gathered from the U.S. Energy Information Administration (EIA) electric power monthly report (U.S. EIA, 2017). The costs for steam and process water are gathered from the SuperPro Designer v9.5 software database. Operating labor cost is assumed to be

20% of the annual operating cost (C_{AOC}); supervisory labor cost is not considered in this study. Other assumptions are obtained from Peters et al. (Peters et al., 2015). Wastewater treatment process costs, research and development (R&D) costs, and distribution and marketing costs have not been considered. Since the depreciation method chosen in this study is the straight-line method, the recovery period for the manufacture of chemicals and allied products is 9.5 years (Department of Treasury, 2018). The salvage value of the purchased equipment is assumed to be zero (Turton et al., 2012).

Table 6.2 Assumptions used to model the annual operating cost (C_{AOC}).

Parameters	**Assumptions**	**Sources**
1. Materials cost (C_M)		
Glycerol	1.04 $/kg	Landress, 2018
Acrylic acid	0.90 $/kg	Molbase, 2018
Phenothazine (PTZ)	11.30 $/kg	Molbase, 2018
Amberlyst 15	104.00 $/kg	Molbase, 2018
Ethanethiol	5.48 $/kg	Molbase, 2018
Carbon disulfide	1.37 $/kg	Molbase, 2018
3-chloro-2-butanone	35.22 $/kg	Molbase, 2018
Acetone	0.10 $/kg	Molbase, 2018
Azobisisobutyronitrile (AIBN)	5.81 $/kg	Molbase, 2018
4, 4’- Azobis	565.00 $/kg	Molbase, 2018
Potassium hydroxide (KOH)	1.05 $/kg	Molbase, 2018
Isosorbide	71.00 $/kg	Molbase, 2018
Succinic anhydride	5.00 $/kg	Molbase, 2018

Table 6.2. (continued)

Parameters		Assumptions	Sources
2. Utilities cost (C_U)			
	Electricity	5.08 cents/kWh	EIA, 2018
	Steam	12.00 $/MT	SuperPro Designer
	Process Water	0.12 $/MT	database
3. Labor cost (C_L)			Peters et al., 2015
4. Facility cost (C_F)			
	Maintenance	0.02* C_{PC}	Peters et al., 2015
	Depreciation	Straight-line method	Peters et al., 2015
	Insurance	0.01* C_{DFC}	Peters et al., 2015
	Tax	0.02* C_{DFC}	Peters et al., 2015
	Plant overhead	0.50* C_L	Peters et al., 2015

Profitability analysis

The gross profit (Eq. 6.3), net profit (Eq. 6.4), return on investment (ROI) (Eq. 6.5), payback time (Eq. 6.6), unit production cost (Eq. 6.7) and net present value (Eq. 6.8), have been calculated based on revenues.

$$Gross\ profit = Revenues - C_{AOC} \quad \text{(Eq. 6.3)}$$

$$Net\ profit = Gross\ Profit - Taxes + Depreciation \quad \text{(Eq. 6.4)}$$

$$Return\ on\ investment\ (ROI) = \frac{Net\ profit}{Total\ investment} \times 100 \quad \text{(Eq. 6.5)}$$

$$Payback\ times\ (in\ years) = \frac{Total\ investment}{Net\ profit} \quad \text{(Eq. 6.6)}$$

$$Unit\ production\ cost = \frac{Annual\ total\ investment}{Unit\ reference\ flow} \quad \text{(Eq. 6.7)}$$

$$Net\ present\ value\ (NPV) = \sum_{t=1}^{T} \frac{C_t(Net\ cash\ flow\ at\ period\ t)}{(1+discount\ rate)^t} - C_0 \quad \text{(Eq. 6.8)}$$

Uncertainty analysis

Sensitivity analysis was performed to investigate potential variation in the product value due to input variable variation (Saltelli et al., 2008). In this study, several variables were chosen based on their potential impact on product value, including capital cost, several raw materials cost, and labor cost.

In addition to sensitivity analysis, scenario analysis has also been performed to explore the uncertainty associated with the TEA study. In this study, we investigated best-case scenario and worst-case scenario with regard to three parameters: total capital investment, glycerol origins, and PSA's selling price.

Discounted cash flow (DCF) analysis

By considering the time value of money, discounted cash flow analysis is required in order to obtain a more accurate production price. All cost results in this study, including the equipment cost and raw materials price, are presented in 2016 dollars. The discount rate is set as 10%, which is a commonly-used value in the literature (Li et al., 2015; Swanson et al., 2010), and the assumed plant life is 15 years. The assumed federal income tax rate is 40% (SmartAsset, 2018). The minimum selling price (MSP) for this PSA is calculated by setting net present value (NPV) to zero.

Results and discussion

Economic analysis results

The total capital investment, annual operating cost, revenue, and unit production cost for all five scales are shown in Table 6.3. As expected, a larger plant scale requires higher capital investment and higher operating cost, and in turn it can provide higher revenues and a lower unit production cost.

Table 6.3 Economic analysis results of the five scales.

Scale (t/d)	Total Capital Investment ($)	Annual Operating Cost ($)	Revenue ($)	Unit Production Cost ($/kg)
1	48,909,738.49	3,876,334.46	1,457,553.21	19.37
2	51,057,911.03	4,845,825.31	2,937,543.67	11.79
5	53,681,083.09	6,393,394.10	7,348,741.19	5.73
10	55,937,859.86	10,313,591.09	14,705,087.74	4.07
40	62,293,006.46	33,506,922.88	58,801,353.76	2.76

The total capital cost of the largest plant scale (40 t/d) were estimated to be $62 million. As discussed in *Methods*, the total capital investment (C_{TCI}) is composed of three major parts: direct fixed capital cost, working capital, and start-up cost. Table 6.4 presents the direct fixed capital cost (C_{DFC}) of the 40 t/d PSA production plant. The stirred reactor is reported to be the most expensive item among all the equipment since it is used in most neutralization, purification, and production and polymerization process.

Table 6.4 Direct fixed capital cost (C_{TCI}) of the 40 t/d PSA production plant.

Items	**Cost ($)**
Equipment purchase costs	6,293,000
Process piping	4,279,240.00
Instrumentation	3,146,500.00
Insulation	188,790.00
Electrical facilities	1,887,900.00
Buildings	2,831,850.00
Yard improvement	1,258,600.00
Auxiliary facilities	3,461,150.00
Installation	2,643,100.00
Land	503,440.00
Engineering and supervision	7,948,071.00
Construction expenses	9,272,749.50
Contractor's fee	2,622,863.43
Contingency	3,497,151.24

The annual operating cost (C_{AOC}) is composed of material cost, utilities cost, labor cost and facilities cost as presented in Table 6.5. Utility consumption from SuperPro Designer v9.5 software and current raw materials marketing price are used to calculate the C_{AOC}. As illustrated in Table 7.5, materials is reported to be the most expensive item (around 68% of the annual operating cost). This is consistent with most of the TEA studies that assert that raw materials frequently are the largest operating cost. It is noticed that the AG production process was the largest expenditure (as shown in Fig. 6.8), contributing to nearly 60% of the total operating cost in the 40 t/d PSA production plant. This is because this

process produces the monomer and requires massive amounts of glycerol and acrylic acid as well as catalysts.

Table 6.5 Annual operating cost of the 40 t/d PSA production plant.

Items	**Cost ($)**
Materials	24,948,842.36
Utilities	182,599.52
Labor	6,092,167.80
Maintenance	125,860.00
Depreciation	662,421.05
Miscellaneous	1,495,032.16

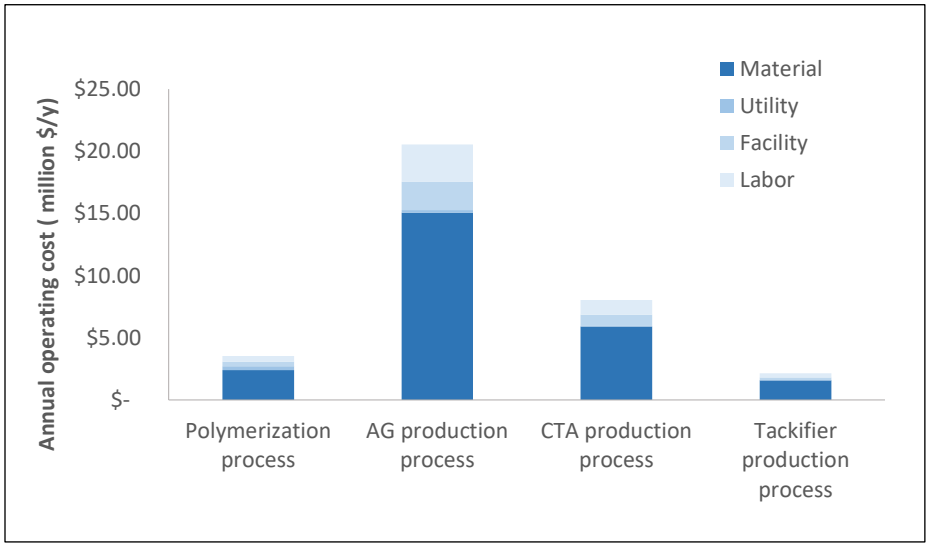


Figure 6.8 Annual operating cost ($) distribution of 40 t/d PSA production plant.

The unit production cost ($/kg) of bio-adhesives for the five scales are shown in Fig. 6.9. In accordance with expectation, increasing plant scale will result in decreasing unit production price. The lowest unit cost obtained in this study is $2.76 /kg in the 40 t/d PSA

production plant. The trend line from the smallest plant to the largest one follows Eq. 6.10 with R^2= 0.95:

$$\text{Unit cost (\$/kg)} = 16.62 \times \text{Plant Scale (t/d)}^{-0.54} \quad \text{(Eq. 6.10)}$$

The lowest unit cost calculated in this study is slightly lower than the current marking price (U.N. Comtrade, 2018), possibly explained by the fact that the system boundary in this study is gate-to-gate; in other words, upstream and downstream processing costs were not used to calculate the unit production cost.

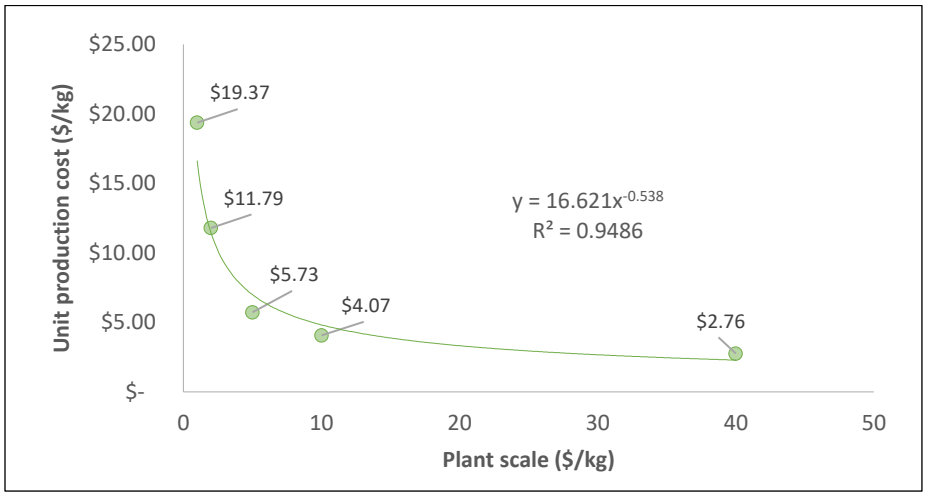


Figure 6.9 Unit production cost ($/kg) of PSA in different scales.

Sensitivity analysis results

As illustrated in Fig. 6.10, the material cost is the most sensitive variable in terms of the unit production cost among all input variables. This implies that material cost drives the PSA production process developed in this study. By exploring the raw materials used in this research, it is found that the price of glycerol, acrylic acid, and catalyst are the most sensitive factors, and changes in any of these three materials will result in changes in the final product price (from $2.54 /kg to $2.99 /kg).

Capital cost is another important variable due to the uncertainty associated with the study. As discussed in previous, the changes of the total capital investment (C_{TCI}) has the second largest influence on the final product price, followed by working capital and startup cost. Except for material cost and capital cost, we found that labor cost is also quite critical in this study, suggesting that if administrative cost and supervisory cost are considered, the final product price may increase to $2.82 /kg. In addition, if we adjust the discount rate from 0 to 15%, the minimum selling price rises from $2.76 /kg to $3.85/kg as shown in Fig. 6.11.

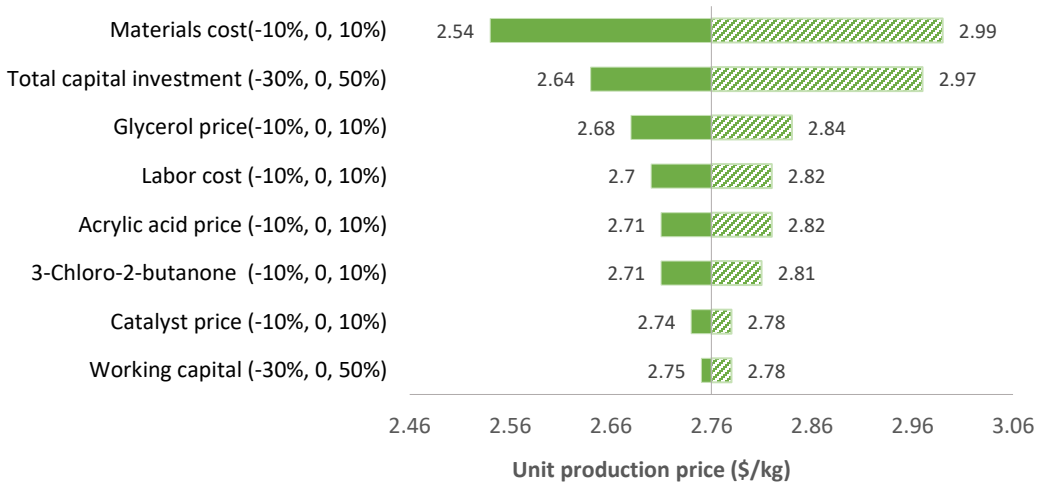


Figure 6.10 Sensitivity analysis of the 40 t/d PSA production plant.

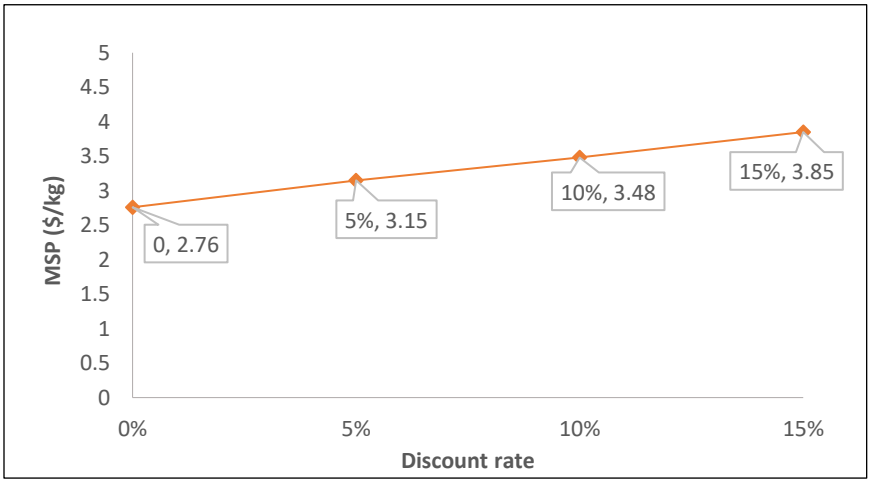


Figure 6.11 Influence of discount rate on MSP of the 40 t/d PSA production plant.

Scenario analysis results

Three scenario analysis has been conducted due to the uncertainty associated with the TEA study. First of all, we investigated the best-case and worst-case scenarios when changing the capital investment (Fig. 6.12). It is found that in best-case scenario (C_{TCI} decreased by 30%), the unit production price may be reduced to $2.68/kg. And this price may be increased to $2.90/kg in worst-case scenario (C_{TCI} increased by 50%). However, in terms of net profit and gross profit, there is little difference between base-case scenario and worst-case scenario.

Secondly, we explored the sources of glycerol. In this study, glycerol is produced from the biodiesel plant. Another way to produce glycerol is through petroleum refinery. Due to the low price of glycerol from crude oil plant ($0.20 /kg vs. $1.04 /kg), it has widely applications than that from biodiesel plant. Even though the unit production reduces to $2.11 /kg (Fig. 6.13), the associated environmental impact increases 35% (Sheehan et al., 1998).

Third, we explored the selling price of structural bio-adhesive. Depending on its application, adhesive's selling price varies largely. Based on the U.N. commodity data, the worst-case scenario and best-case scenario were chosen between +50% to -50%. As shown in Fig. 6.14, in the worst-case scenario, both gross profit and net profit are negative, which indicating no profit will be gained in this situation. While in best-case scenario, the payback time decreases to nearly 2 years. And the gross profit and net profit doubles in best-case scenario.

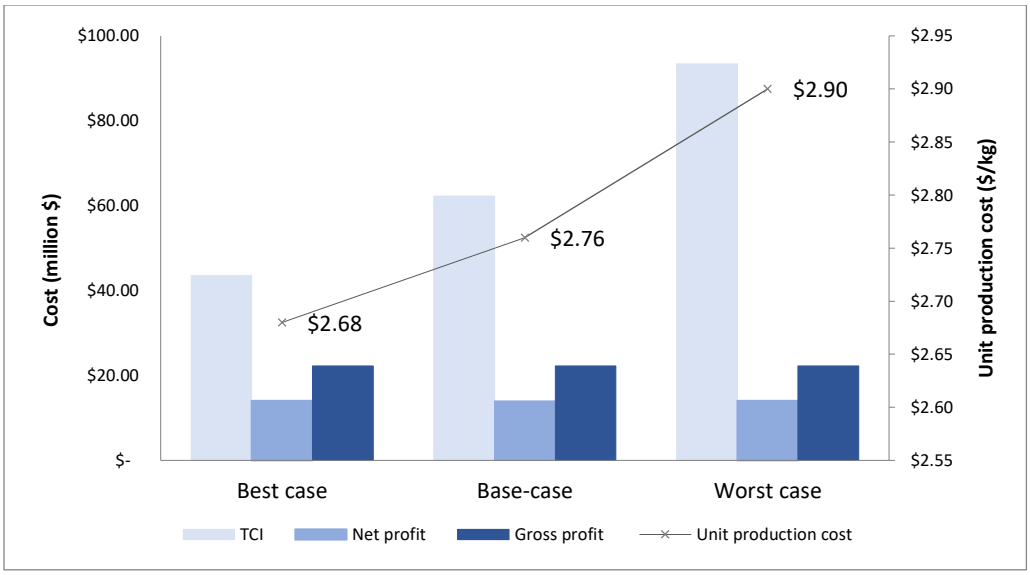


Figure 6.12 Scenario analysis result of the total capital investment for the 40 t/d PSA production plant.

Figure 6.13 Scenario analysis result of the glycerol sources for the 40 t/d PSA production plant.

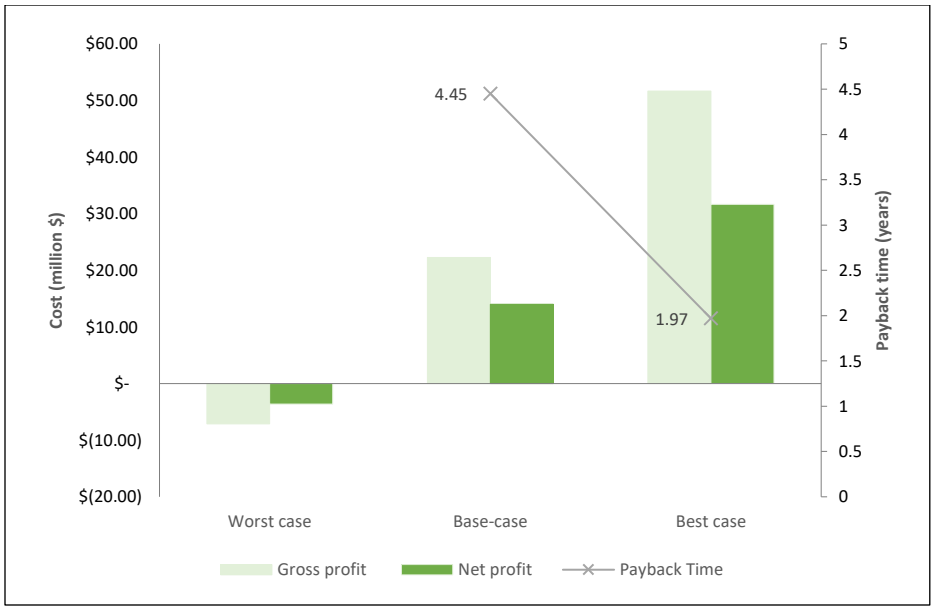


Figure 6.14 Scenario analysis result of the PSA selling price for the 40 t/d PSA production plant.

Discount cash flow (DCF) analysis

Fig. 6.15 depicts the cumulative discounted after-tax cash flow of the 40 t/d PSA production plant at various discount rates (i). Table 6.6 summarizes the economic performance of the 40 t/d PSA production plant in terms of revenue, net profit, ROI, NPV, IRR and payback time. If the time value of money is considered, the net present value (NPV) decreases from 143.2 million dollars to 27.4 million dollars at the end of the project (i = 10%). With a higher discount rate, the NPV decreased accordingly (NPV= 4.7 million dollars when i = 15%). The internal rate of return (IRR) is 16.50% as calculated, so this project is acceptable because IRR is larger than the discount rate (10% as assumed in *Methods*). In addition, the 40 t/d plant was found to be profitable as indicated by the positive NPV. As for the minimum selling price (MSP), if NPV is zero and the price of the structural bio-adhesive is varied, the MSP is determined to be $3.48 /kg when the discount rate is 10%.

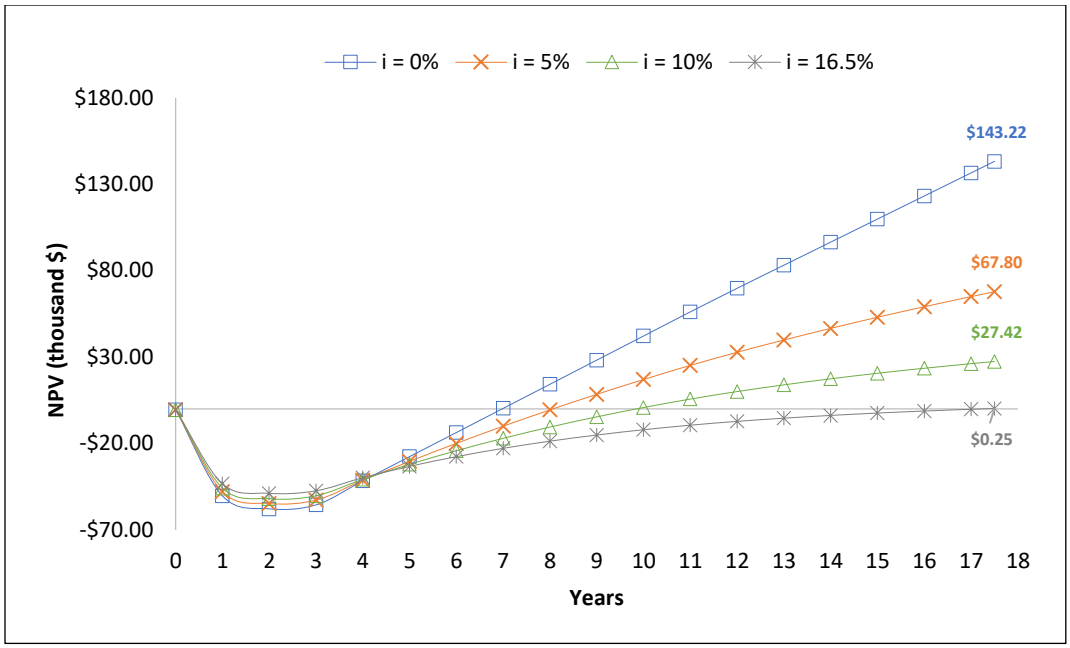


Figure 6.15 Discounted cash flow result of the 40 t/d PSA production plant at different discount rate.

Table 6.6 Profitability indicators of 40 t/d PSA production plant at discount rate of 10%.

Items	**Scale: 40 t/d**
Revenue ($/y)	58,801,353.76
Net profit ($/y)	14,011,429.25
Return on investment (%)	22.49%
Payback time (y)	9.2
Net present value ($)	27,422,423.39
Internal rate of return (%)	16.5
Minimum selling price($/kg)	3.48

Conclusions

A techno-economic analysis (TEA) study was conducted to explore the economic feasibility of a pressure sensitive adhesive from reversible addition-fragmentation chain transfer polymerization (RAFT) process. In total, five plant scales were modeled in SuperPro Designer. The lowest unit production price obtained in this study is $2.76 /kg of a 40 t/d PSA production plant. We found that the raw material costs were the most sensitive parameter with respect to the product value. Furthermore, based on the cash flow analysis, it is found that this project should be accepted due to its positive IRR. The minimum selling price is determined to be $3.48/kg. Given the uncertainty associated with TEA study, it is recommended that a more detailed project analysis could be conducted to further explore the performance of this PSA production process.

Acknowledgements

This study was funded by the National Institute of Food and Agriculture of the United States Department of Agricultural, under the project number 214-38202-22318.

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CHAPTER 7. CRADLE TO GATE LIFE CYCLE ASSESSMENT OF TRADITIONAL FORMALDEHYDE-BASED ADHESIVES USED IN WOOD PRODUCTS

Modified from a paper to be submitted to *Industrial Crops and Products.*

Abstract

Traditional formaldehyde-based adhesives still play a crucial role in the current market despite increasing environmental concerns resulting from their production. The purpose of this paper was to evaluate the environmental effect of formaldehyde-based adhesives mainly used for wood products. In this study, a functional unit (FU) of 1kg adhesive was used. GaBi 6 software were employed to perform the life cycle assessment (LCA). Several key parameters for life cycle analysis were analyzed, such as global warming potential, acidification potential, eutrophication potential, and human health. The environmental impact evaluation was conducted between two formaldehyde-based adhesives: urea formaldehyde adhesives (UF adhesives) and phenol formaldehyde adhesives (PF adhesives). As a result, the greenhouse gas (GHG) emissions range from 2.04 kg CO_2-eq/FU of UF adhesives to 2.88 kg CO_2-eq/FU of PF adhesives. In terms of the overall environmental impacts, it was found that UF adhesives have a nearly 50% higher life cycle impact than PF adhesives. Comparing the energy consumption used in UF adhesives and PF adhesives, UF adhesives were much lower than PF adhesives. Electricity source was determined to be the most sensitive parameters with respect to global warming potential for formaldehyde-based adhesive. Underlying issues were also discussed in this study.

Keywords

Life cycle assessment (LCA); Urea formaldehyde adhesive (UF adhesive); Phenol formaldehyde adhesive (PF adhesive).

Introduction

Traditional adhesives, such as urea formaldehyde (UF) adhesives and phenol formaldehyde (PF) adhesives, are typically derived from petroleum refinery plant. Formaldehyde-based adhesives were introduced to the market in the early 20th century (Petrie, 2007). In a few years, this market has grown rapidly worldwide. There are more than 14 billion tons of adhesives consumed in the world every year (Ceresana, 2018). Formaldehyde-based adhesive is one of the most widely used polymeric adhesives in the manufacturing industries, especially in wood production (Pizzi and Mittal, 1994). Approximately 1 million metric tons of UF adhesive is produced every year, and the global market value of adhesives is estimated to be $59.75 billion by 2020 (Markets and Markets, 2015).

In the early stage, adhesives and sealants were collected from animals and plant without processing, much of the animal glues were used as interior applications. As the development of new technologies, synthetic adhesives became the predominant ones because of their advantages of low cost, water resistance, and easy accessibility. After World War II, the employment of UF adhesives has led to the expansion of existing interior products as well as the development of the new panel products (Salthammer et al., 2010).

In the wood products industries, adhesives play a vital role in making the wood products more efficient and productive. UF adhesive was the first synthetic adhesive that has been used for wood bonding application (Keimel, 2003). More than 70% of UF adhesives are

used for manufacturing a variety of products, such as plywood, particleboard, and medium density fiberboard (Frihart, 2015). UF adhesives have many advantages that made them popular worldwide up to date. For example, UF adhesive is colorless when applying on the surface of wood; UF adhesive has good strength performance that can fulfill the requirements; more importantly, due to the low price of UF adhesive, it can be applied in large scale manufacturing with less economic burdens (Nuryawan et al., 2016).

PF adhesives are commonly used in plywood manufacturing. Not only can it provide high strength, but also the water resistance characteristic of PF adhesive prevents delamination and has better temperature stability (Çetin and Özmen, 2002). Even though PF adhesives are considered to have lower free formaldehyde emission as compared with UF adhesives (Messmer and Chaudhary, 2015), their selling price can be high due to the flexible cost of phenol.

The common synthetic process of formaldehyde-based adhesive is completed by the reaction of urea or phenol with formaldehyde (Mahendran et al., 2010). With proper formaldehyde to urea (F/U) or formaldehyde to phenol (F/P) molar ratio, adhesives can accomplish the requirements entirely. Theoretically, the more formaldehyde contained in the adhesives, the better performance of adhesives may be achieved due to the higher content of reactive groups. But higher amount of formaldehyde could lead to higher emissions. Therefore, the ideal molar ratio of F/U ranges 0.9:1 and 1.1:1 (Messmer and Chaudhary, 2015). Final formaldehyde-based adhesives are usually made in liquid form; powdered type is sold as well for some special applications (Dunky, 2004).

The concerns over the depletion of the fossil fuel resources and the environmental impacts of petro-products increased in recent decades, especially the use of formaldehyde-

based adhesives (McDevitt and Grigsby, 2014). The emissions of volatile organic compounds (VOCs) from the formaldehyde-based adhesives may contaminate the environment. Some of the environmental regulator has set the exposure limitation for the components which may cause environmental burdens to the environment. For instance, the United Kingdom, China, and Japan set the limit of 0.1 mg/m^3 of formaldehyde emission; while in Canada, Germany, and Singapore, 0.123 mg/m^3 of formaldehyde emission is adopted (Petrie, 2007).

In order to effectively quantify the environmental consequences, life cycle assessment (LCA) has been introduced to solve the problem. LCA is a systematic tool involving the entire life cycle stages: raw materials acquisition, manufacturing, product usage, recycling and disposal; the environmental impacts at each stage have been quantified by LCA. Environmental life cycle assessment has been first applied in the 1970s (Hocking, 1991). Subsequently, the application of LCA has been widely encouraged by the governments around the world, as well as the industry organizations.

Based on the International Organization Standardization (ISO) 14040 standards, LCA has four steps: goal and scope definition, life cycle inventory analysis, life cycle impact assessment, and interpretation (ISO, 1997). By conducting LCA, the environmental impacts at various phases could be identified; it could not only help to meet the air quality requirement, but also help decision makers with process design and project management.

In this research, the authors intend to investigate the cradle-to-gate life cycle assessment of formaldehyde-based adhesives, more specifically, urea formaldehyde (UF) adhesives and phenol formaldehyde (PF) adhesives, which could be used in wood products. These two adhesives will be compared in terms of detailed environmental impact categories

like greenhouse gas (GHG) emission, air pollutions and toxic releases, and the overall environmental impacts. Its energy requirement was also analyzed in this study.

Methodology

Goal and scope definition

The focused goal of this research is to assess the potential life cycle environmental impacts and resources consumptions of formaldehyde-based adhesives' production. This paper primarily aims to answer the following questions:

1) Which kind of formaldehyde-based adhesives, UF adhesive or PF adhesive, has higher environmental impacts?

2) How does the adhesives' production process affect the environmental impact categories?

The simplified system boundary for both scenarios is shown in Fig. 7.1. This study is a cradle-to-gate LCA analysis, thus the system boundary is considered from raw materials extraction to adhesive production process. Two types of scenarios are considered in this study: 1) urea formaldehyde (UF) adhesives and 2) phenol formaldehyde (PF) adhesives. Depending on the scenarios considered, the life cycle stages involve slightly difference production process. The functional unit (FU) used in this study is the production of 1 kg adhesive with 100% solids content.

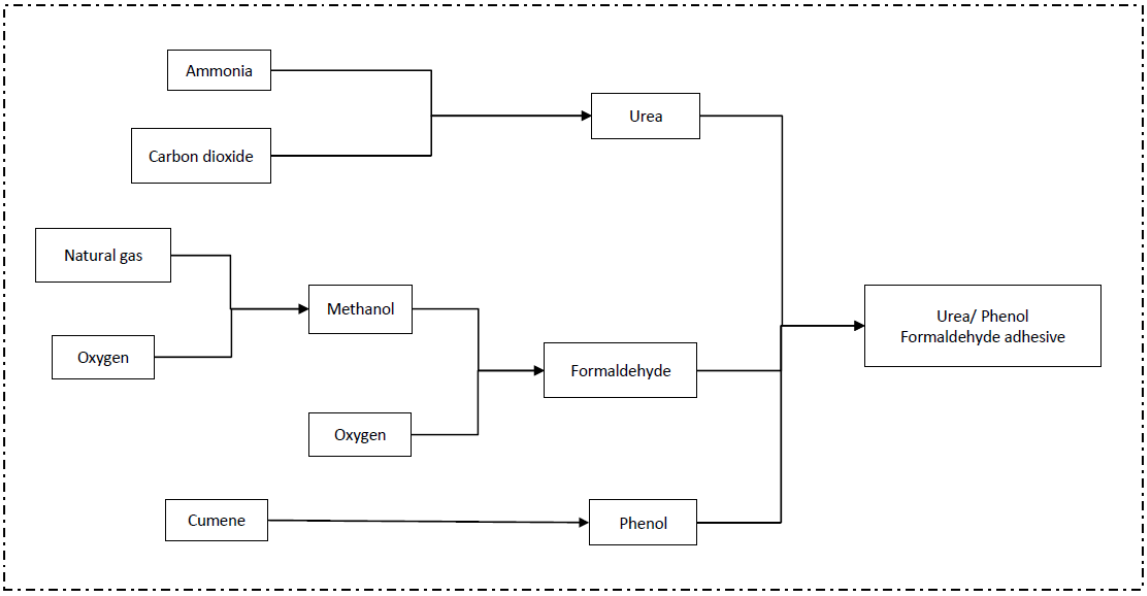

Figure 7.1 System boundary and production process of PF adhesives and UF adhesives.

Life cycle inventory analysis

Under the guidance of ISO 14040, data collection process follows the consistency, accuracy, and geographical specifications. Data on urea and formaldehyde production was taken from the Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) database developed by U.S. Argonne National Lab (Argonne National Lab, 2015). And data on urea formaldehyde adhesive and phenol formaldehyde adhesive production were collected from Consortium for Research on Renewable Industrial Materials reports (CORRIM, 2013). Furthermore, GaBi 6 database was used in calculating emissions associated with oil and natural gas extraction and transportation. Eco-Invent database was also adopted in estimating the emissions and calculations. Major resource assumptions are listed in Table 7.1.

Table 7.1 Major resource assumptions of formaldehyde-based adhesives production.

Life cycle stage	**Assumption**	**Data source**
Crude oil extraction and refinery processes	Crude oil were provided from the Middle East, and transported to U.S. by ocean freight and pipeline as well.	GaBi 6 database
Chemical production processes	Urea, phenol and formaldehyde was produced from the local factory in Iowa and transported by the diesel powered truck.	GREET, US. LCI database and literatures
Adhesives production processes	Adhesives production plant was located in the center of Iowa	Patents and reports

Table 7.2 shows the electricity sources in Iowa reported by the U. S. Energy Information Administration (U. S. EIA) (EIA, 2016). In Iowa, nearly 60% of the electricity was generated by fossil fuels. And the renewable sources contributed to 35% of the electricity. In this study, it is used in assessing energy consumptions of traditional formaldehyde-based adhesives' production.

Table 7.2 Electricity sources in Iowa, 2016.

Energy source	**Percentage**
Fossil fuels	57.83%
Hydroelectric	17.81%
Wind	13.82%
Nuclear	3.65%
Wood and wood-derived fuel	2.41%
Solar Photovoltaic	1.95%
Geothermal	1.01%
Landfill gas	0.67%
Biogenic municipal waste	0.44%

The adhesives production process was built in GaBi 6 software. Formaldehyde is produced the same way in both UF adhesives and PF adhesives as oxidation of methanol using metal oxide catalyst pathway at around 350°C (ICIS, 2018).

Urea is produced from the reaction of carbon dioxide (CO_2) and ammonia (NH_3). When producing UF adhesives, the molar ratio of formaldehyde to urea is set to1.09 (Wilson, 2009). Phenol is produced from oxidation of cumene at a temperature of about 80°C. This process is known as Hock process. Propane is the co-product from the production of phenol, but it is not considered in this study. PF adhesives use the molar ratio between formaldehyde to phenol (F/P) of 2.3 (Wilson, 2009).

As for the transportation distance, the adhesive production plant is assumed to locate in central Iowa. It is assumed 150 miles for urea/phenol production plant to adhesives production plant, and 50 miles from formaldehyde plant to adhesives production plant.

Life cycle impact assessment

GaBi 6 software is employed in the life cycle impact assessment in order to evaluate the potential environmental impacts of formaldehyde-based adhesives production process. The impact assessment methods chosen for this study are the Tool for the Reduction and Assessment of Chemical and other environmental Impacts (TRACI) and Eco-Indicator 99 (EI-99). TRACI is an impact method developed by U.S. Environmental Protection Agency (U.S. EPA), and it contains impact categories such as ozone depletion, global warming, acidification, eutrophication, ecotoxicity, photochemical oxidation, and human health criteria (EarthShift, 2014). The potential environmental impacts are calculated at every stage across the entire life cycle. EI-99 is an end-point impact assessment method expressed in one single score: human health impact, ecosystem quality, and resource depletion (Dreyer et al., 2003).

Sensitivity analysis

Sensitivity analysis is adopted to explore the sensitive input parameters with respect to GHG emission, expressed as global warming potential (GWP). Two input variables were chosen based on their potential environmental impacts: electricity sources and transportation distances. The reason for choosing electricity sources is due to the preliminary environmental impact exploration on replacing current electricity sources with 100% renewable sources and 100% fossil fuel sources. As for transportation distance, it is considered as a sensitive factor because the transportation vehicle is powered by diesel.

Results and discussion

The energy consumption of producing one functional unit (FU) product are shown in Fig. 7.2. The amount of the energy input was 68 MJ/FU for UF adhesives production, and 123 MJ/FU for PF adhesives production process. Among all the energy categories, natural gas is reported as the largest contributor to the overall energy consumption since it is mainly used for generating steam.

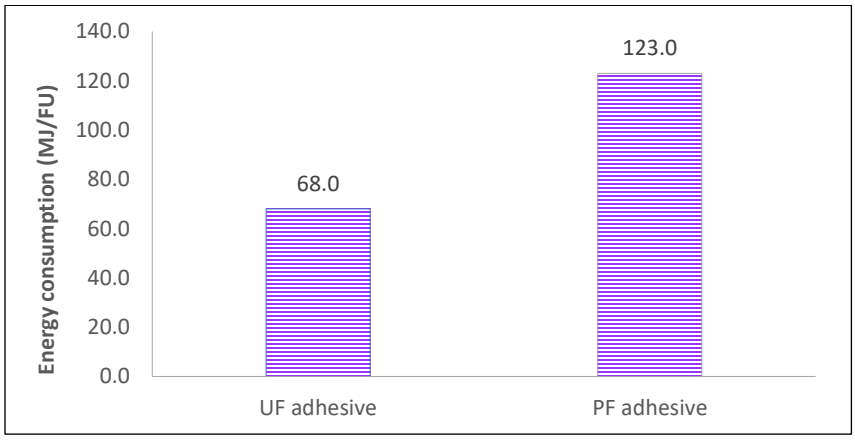

Figure 7.2 Energy consumption of UF adhesives and PF adhesives production process.

Global warming potential (GWP), acidification potential (AP) and eutrophication potential (EP) results of UF adhesives and PF adhesives production process are shown in Fig. 7.3, Fig. 7.4 and Fig. 7.5. Global warming potential measures the effects of GHG emissions in relation to carbon dioxide. The acidification process usually occurs through transformation of air pollutants into acids; and the eutrophication process primarily refers to the enrichment of nutrients in the certain place, such as aquatic or terrestrial.

As indicated in Fig. 7.3, UF adhesives production process produced less global warming air compared with PF adhesives production process (2.04 kg CO_2-eq./FU for UF adhesives and 2.88 kg CO_2-eq./FU for PF adhesives); not surprisingly, UF adhesives production process could recycle CO_2 as materials and less energy was consumed, which led to the lower global warming air result. In addition, less amount of formaldehyde was used to produce UF adhesives, therefore less global warming air was produced through UF adhesives' process than PF adhesives'.

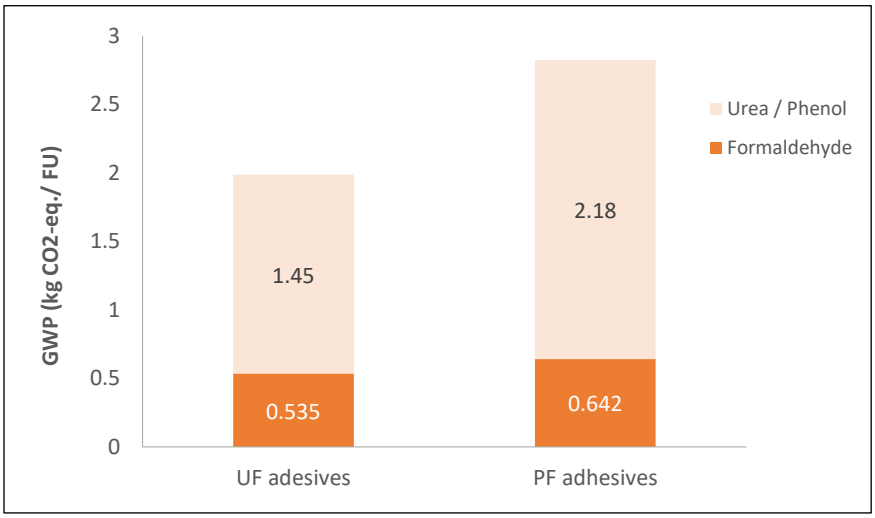

Figure 7.3 Global warming potential results of UF adhesives and PF adhesives production process.

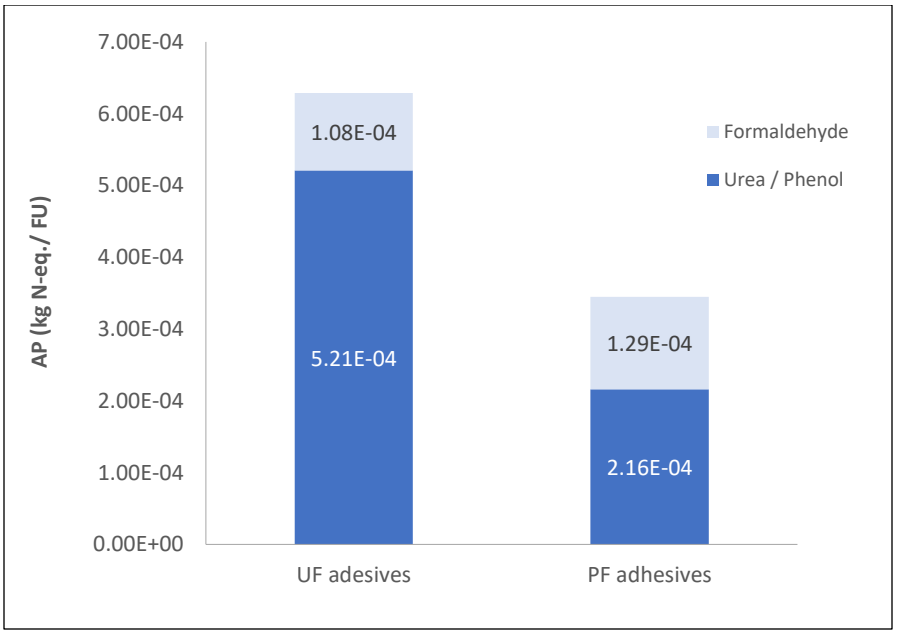

Figure 7.4 Acidification potential results of UF adhesives and PF adhesives production process.

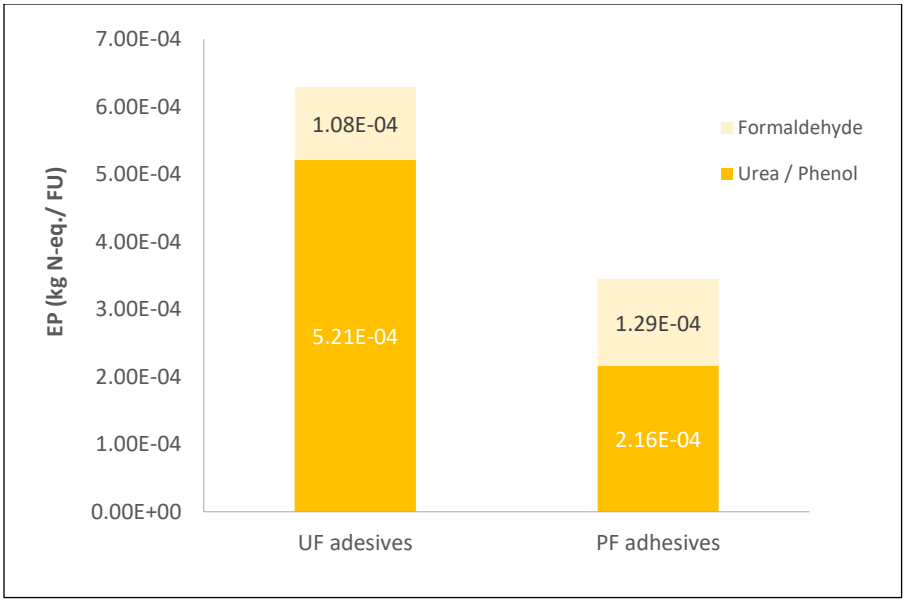

Figure 7.5 Eutrophication potential results of UF adhesives and PF adhesives production process.

As shown in Fig. 7.4, the total AP of UF adhesives was 1.34 kg H+ moles- eq./FU, and total AP of PF adhesives was 1.14 kg H+ moles- eq./FU. UF adhesives production process has larger environmental effect because more urea was used to produce UF adhesives. Urea and phenol production process contributed the most of the acidification air.

EP results for both UF adhesives and PF adhesives are shown in Fig. 7.5. The EP of UF adhesives was 6.38E-04 kg N- eq./FU, and the eutrophication potential of PF adhesives was 3.55E-4 kg N- eq./FU. In both UF adhesive and PF adhesive's production processes, the urea and phenol production process has larger eutrophication air potential than formaldehyde production process, which is 5.21E-04 kg N-eq./FU and 2.16 E-04 kg N-eq./FU, specifically.

In Fig. 7.6, the smog air effect results of UF adhesives and PF adhesives were exhibited. For UF adhesives, the total smog air emission was 4.34E-02 kg O_3-eq./FU; among which urea production process occupied the most (2.85E-02 kg O_3-eq./FU). The total emission of PF adhesives was 7.41E-02 kg O_3- eq./FU. Result from PF adhesives production process is larger because the production of phenol requires larger input from petroleum refinery, which leads to higher smog air emission.

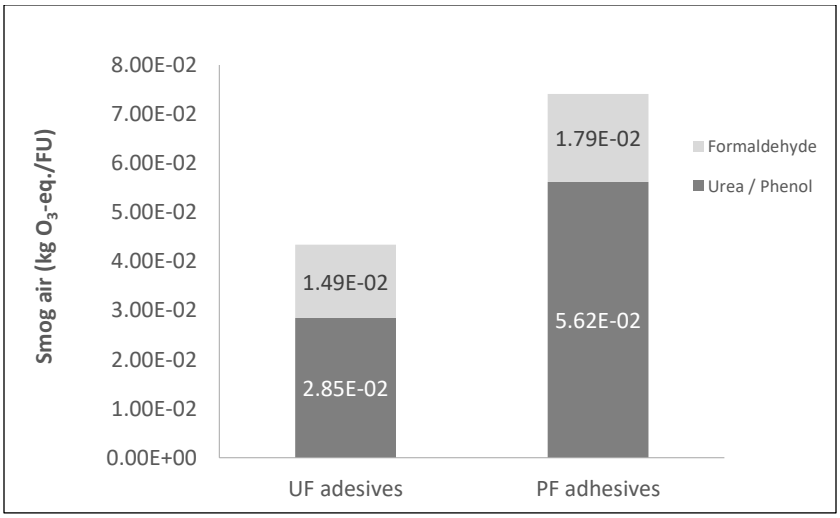

Figure 7.6 Smog air results of UF adhesives and PF adhesives production process.

The ozone depletion potential (ODP) result for both UF adhesives and PF adhesives are shown in Fig. 7.7. The ODP of UF adhesives was 3.62E-12 kg CFC 11- eq./FU, and the ODP of PF adhesives was 2.25E-11 kg CFC 11- eq./FU. In UF adhesives and PF adhesives production process, urea and phenol production process emitted the most chlorofluorocarbon (CFC) equivalent air. Similar explanation as smog air result is used in higher ODP result in PF adhesives than UF adhesives.

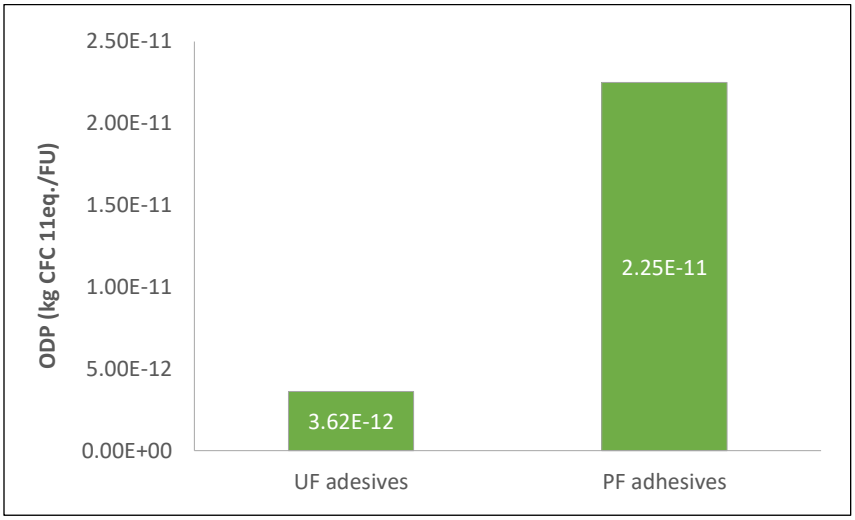

Figure 7.7 Ozone depletion potential results of UF adhesives and PF adhesives production process.

The human toxicity result (cancer effects) (7.28E-07 CTUh/FU of UF adhesives vs. 9.88E-09 CTUh/FU of PF adhesives) indicated that the production process of UF adhesives has higher potential in affecting human health compared with PF adhesives. In addition, UF adhesives production process emitted most of the toxicity air that affects human health, and PF adhesives production processes has produced more contaminated soil that may influence human health. As Ye et al. indicated in 2012, the emission of the hazardous during adhesives production is the major disadvantages of UF adhesives, and they suggested exploring an effective way to eliminate the amount of emission, such as using phenol and polyvinyl

acetate (PVA) as formaldehyde scavengers (Ye et al., 2012). This has been investigated and proved by Kim and Kim in 2005 as well (Kim and Kim, 2005).

As for human toxicity non-cancer effects, the results showed that UF adhesives production process has higher impacts (0.57 CTUh/FU of UF adhesives vs. 0.44 CTUh/FU of PF adhesives). Moreover, the human health non-cancer effects in soil aspect were zero in UF adhesives production processes, which may indicate that during UF adhesives production process, little hazardous emissions were released to the soil.

The detailed TRACI impact analysis results of UF adhesives and PF adhesives are reported in Table 7.3. As exhibited in the table, for some life cycle impact assessment categories, such as smog air and ozone depletion, PF adhesives have higher results than UF adhesives. But for other life cycle impact assessment categories, UF adhesives have a higher result than PF adhesives, such as acidification potential and eutrophication potential. This is because PF adhesives produce less acid-based emissions as well as the corresponding transportation processes. Table 7.3 also indicates that UF adhesives production process may be more harmful to human beings due to the higher result in human toxicity impacts.

In order to compare the overall environmental impacts of the two adhesives, Eco-indicator 99 impact method was used: impact categories were integrated into three single factors (human health impact, ecosystem quality and resources depletion) with the weighting of 40%, 40%, and 20%, specifically. The comparison of PF adhesives and UF adhesives are shown in Fig. 7.8 below. As calculated, UF adhesives have a higher impact (6.65 Pt) than PF adhesives (2.84 Pt), a difference of over 50%. As for the three single indicators, human health impact is much larger for the UF adhesives than the PF adhesives; and in terms of the impact on ecosystem quality and resource depletion, the impact from PF adhesive is higher

than UF adhesive. The environmental impacts comparison has not been done in other research as to the authors' knowledge.

Table 7.3 Life cycle impact assessment results from GaBi software (FU: 1kg of adhesive produced)

Impact categories	**UF adhesives**	**PF adhesives**
TRACI global warming [kg CO2-eq/ FU]	2.04	2.88
TRACI acidification [kg H+ moles-eq/FU]	1.34	1.14
TRACI eutrophication [kg N-eq/FU]	6.38E-04	3.55E-04
TRACI ozone depletion air [kg CFC 11-eq/FU]	3.62E-12	2.25E-11
TRACI smog air [kg O_3-eq/FU]	4.34E-02	7.41E-02
TRACI human toxicity, cancer [CTUh/FU]	7.28E-07	9.88E-09
TRACI human toxicity, non-cancer [CTUh/FU]	0.57	0.44

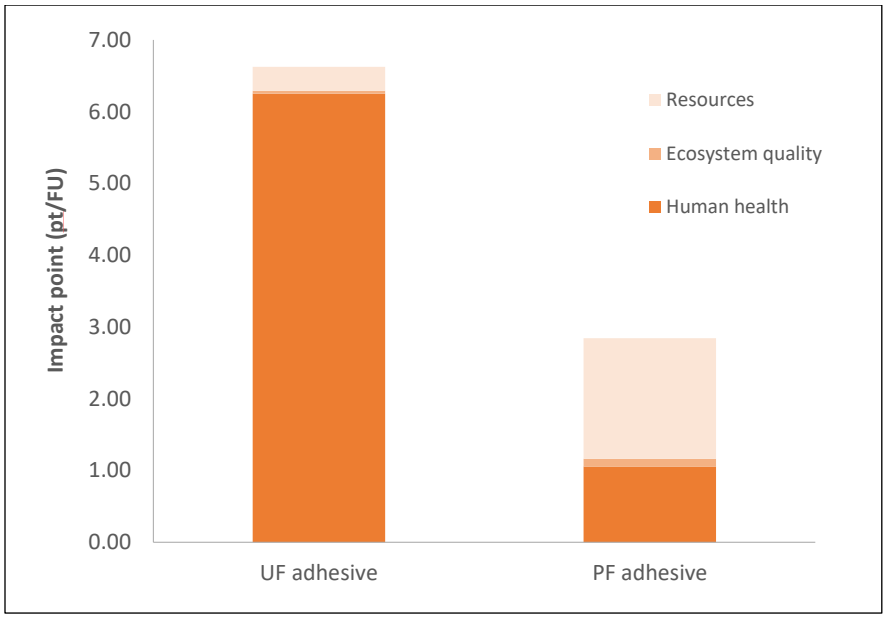

Figure 7.8 Overall life cycle environmental impacts comparison of UF adhesive and PF adhesive production process.

Sensitivity analysis has been conducted on UF adhesives and PF adhesives on transportation distances and electricity sources. As shown in Fig. 7.9, transportation distances resulted in higher impact in terms of global warming potential change in both UF adhesives and PF adhesives. When longer transportation distance is needed (2,000 miles), the GWP increases by 12% due to diesel combustion.

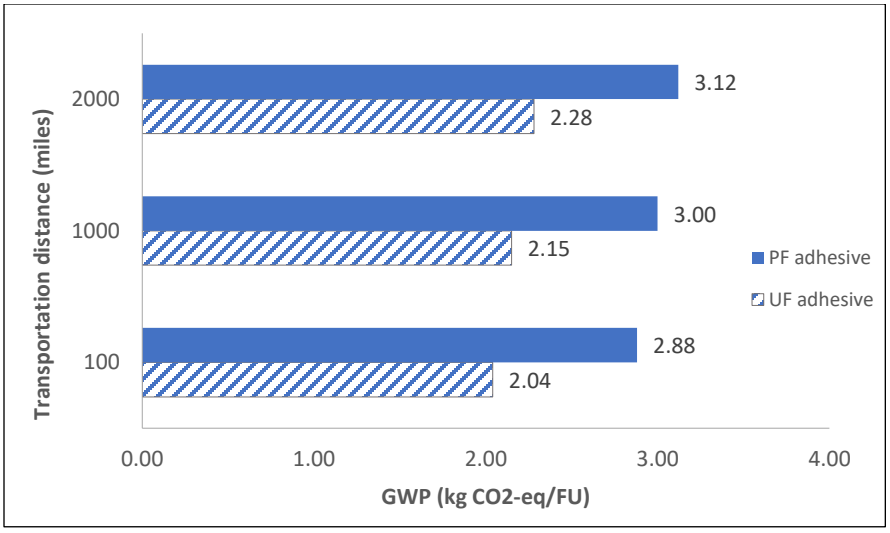

Figure 7.9 Sensitivity analysis of UF adhesives and PF adhesives on transportation distances.

Fig. 7.10 exhibits the sensitivity analysis result on electricity sources. The original GHG emissions in Iowa is 2.04 kg CO_2-eq/MJ of UF adhesives and 2.88 kg CO_2-eq/MJ of PF adhesives. As mentioned in *Methods*, electricity sources in Iowa was composed of nearly 60% of fossil fuels. If the electricity comes from 100% coal, GHG emissions could increase to 2.22 kg CO_2-eq/MJ of UF adhesives and 3.00 kg CO_2-eq/MJ of PF adhesives; on the other hand, if the electricity is 100% renewable sources, GHG emissions reduce to 1.83 kg CO_2-eq/MJ of UF adhesives and 2.74 kg CO_2-eq/MJ of PF adhesives. By replacing the energy source with renewable energy, the environmental impact can be decreased by 10%.

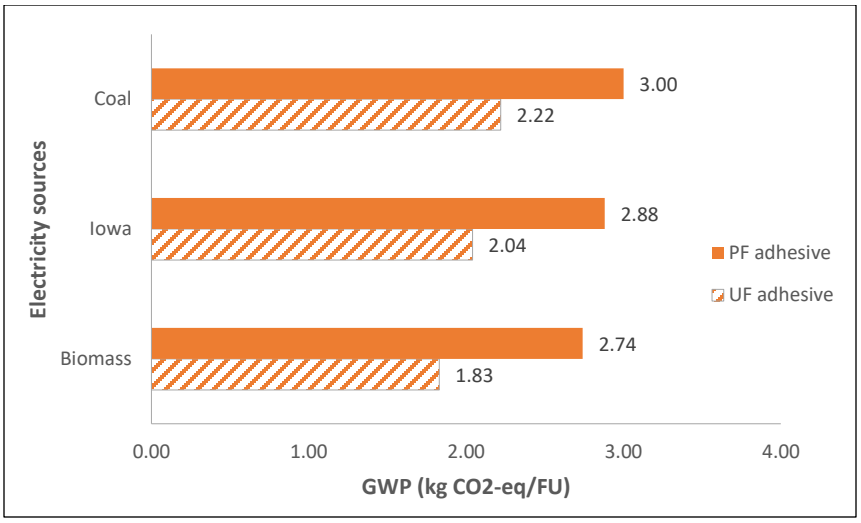

Figure 7.10 Sensitivity analysis of UF adhesives and PF adhesives on electricity sources.

Conclusions

LCA is a valuable tool in assessing the environmental impacts from industrial products. In this study, LCA is adopted to evaluate the cradle-to-gate production processes of urea formaldehyde (UF) adhesives production process and phenol-formaldehyde (PF) adhesives production process. As the results showed, the whole production process of UF adhesives production has lower GHG emissions, but it has the larger influence on human health, acidification and eutrophication aspects. By comparing UF adhesives and PF adhesives production, it was found that even though PF adhesives had higher impacts in ecosystem quality, the overall environmental influence of UF adhesives was larger than PF adhesives. With the rapid development in adhesive markets, environmental impacts of the product would be lesser; and greener and healthier products could be produced from renewable materials.

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CHAPTER 8. TECHNO-ECONOMIC ANALYSIS OF UREA FORMALDEHYDE ADHESIVES USED IN WOOD PRODUCTION

A paper submitted to *Industrial Crops and Products.*

Abstract

Even though there are environmental concerns associated with petroleum-based adhesives production process, they have been used for several decades due to relatively low price and conveniences. The purpose of this paper was to analysis the economic feasibility of urea formaldehyde (UF) adhesives used in wood products. Two formaldehyde production pathways: metal oxide catalyst pathway and silver catalyst pathway, were adopted in this study. SuperPro Designer v9.5 software was employed to perform the techno-economic analysis (TEA). Key parameters of TEA were analyzed, including total capital investment, annual operating cost and revenues. It was found that the unit production price of UF adhesive made from metal oxide catalyst pathway ($0.86/kg) was less expensive than it from silver catalyst pathway ($1.01/kg), but total capital investment was higher in metal oxide catalyst pathway than that of silver catalyst pathway. In addition, sensitivity analysis was performed to evaluate the key factors that may have a large influence on the results. Not surprisingly, product yield and material cost were two of the most sensitive factors among all input parameters.

Keywords

Techno-economic analysis (TEA); Urea formaldehyde adhesive (UF adhesive); Metal oxide catalyst pathway; Silver catalyst pathway.

Introduction

Resins made from urea formaldehyde polymer began commercial use as adhesives in 1920s (Kauffman et al., 1999). Afterwards, urea formaldehyde (UF) adhesives became one of the most widely used plastics worldwide. There are more than 13 billion tons of adhesives produced each year (Ceresana, 2015). As estimated by the United States Department of Agriculture (USDA) Forest Service, approximately more than 70% of UF adhesives are used for bonding purpose in forest product industries, such as medium density fiberboard, hardwood, plywood, and particleboard (Conner, 1996).

UF adhesive is one type of the amino resins. Amino resins are thermosetting resins with excellent tensile strength, hardness and impact resistance (DIC, 2016). Usually, amino resins have the ability of modifying the properties of materials. For example, in textile fabrics production process, it could help to increase the permanent press characteristics. In addition, it could be used in molding products (Skeist, 1990).

UF adhesive is consisted of linear or branched oligomer and polymeric molecules. In industrial production, UF adhesive is made by the condensation of formaldehyde and urea in an aqueous solution. Even though it is composed of only two main components (urea and formaldehyde), the formation reactions of UF adhesive are quite complex. Different conditions and molar ratio of formaldehyde to urea could result in various condensed products. There are usually two steps synthesis reactions. First, urea and formaldehyde react to form mono-methylolurea, di-methylolurea and tri-methylolurea, mostly mono-methylolurea; then, these products are condensed to low molecular weight polymers. The condensation reaction could give a colorless solution that can be dried to a powder. The final product is then distilled until 65% solids content of UF adhesive achieved.

The advantages of UF adhesive includes low curing temperatures and resistance to microorganisms. In addition, it is resistant to many chemicals and the electrical resistance made it desirable for wall outlets and switch plate products (Kauffman et al. 1999). Among all adhesives, UF adhesive is reported as the most economic one (Gürü et al., 2006). However, UF adhesive is less durable than phenol formaldehyde adhesive and lack of resistance to water in exterior applications (Kauffman et al., 1999). Due to the amino-methylene linkage, it is unstable under the moist conditions, especially in combination of heat. Besides, hydrolysis of weakly bound compounds may lead to the reverse reaction, which could result in the formaldehyde emission from the UF-bonded product (Dunky, 1998).

Formaldehyde (CH_2O), one of the most important precursors of many industrial chemicals, has been synthesized in Germany in late 19^{th} century. Several years later, formaldehyde production from mixture of methanol vapor and air became possible in industrial scale. It is found that the ratio of methanol and air as well as the catalyst employed during production has large effect on the yield of the reaction. In 1925, due to the development of methanol production from timber industry, the production of formaldehyde has been truly produced on a commercial scale (Austin, 1984).

Typically, formaldehyde is produced by two main routes: oxidation-dehydration process using silver as the catalyst and direct oxidation of methanol using metal oxide as the catalyst. Silver catalyst is the oldest route, and it is often carried out at high temperature (around 650°C). As estimated in 2000, over 50% of west European companies adopted this pathway in industrial application (Qian et al., 2003). The other process, metal oxide catalyst process is the most widely applied modern commercial process (Gayathri and Muthamilarasi, 2005). This process requires lower temperature (about 350°C) and the generated heat could provide steam for process heating

(ICIS, 2007). In this study, these two routes will be compared in order to find the own strength of each pathway.

The other material, urea ($CO(NH_2)_2$), plays an important role in chemical industries as well. According to Ceresana, one of the market research institutes, the global urea market may increase to $96 billion in 2019 (Ceresana, 2012). German chemist, Friedrich Wöhler, obtained it from the reaction of silver cyanate and ammonium chloride in late 19^{th} century. This has been regarded as a milestone in chemistry because it was the first time that an organic compound was artificially synthesized from inorganic materials. Urea has been broadly applied in agriculture, especially as a fertilizer. It is estimated that urea has the highest nitrogen content among all fertilizers. Besides this characteristic, it is also used in chemical industry, particularly in the manufacturing of UF adhesive and melamine urea formaldehyde adhesive (Austin, 1984).

The debate on UF adhesive has been continued throughout the last decade. Even though the limit of free formaldehyde emission has been revised, the side-effect of UF adhesive is still a concern by public (Que et al., 2007). Biobased adhesives have been explored in these days in order to make more environmentally friendly product. However, no thorough comparison between formaldehyde adhesive and biobased adhesive has been studied in both economic and environmental perspectives.

Techno-economic analysis (TEA) is a process-modeling tool to simulate the production process in the system level. TEA not only includes the technical parameters, but also economic factors into the project (Chau et al., 2009). It starts with the material and energy balance, and then cost analysis is conducted to assess the economic feasibility of the product. As a simulation tool, the assumptions of the study are highly important. Different assumptions could lead to significantly different results (Coker, 2011).

The objective of this study is to evaluate the economic value of UF adhesive production process. Two different pathways to produce formaldehyde (silver catalyst pathway and metal oxide catalyst pathway) will be explored in this study. Production efficiency, total capital cost, annual operating cost, unit production cost, as well as payback time will be quantified in this study. Comparisons will be made between these two pathways in the above perspectives.

Methods

In this study, SuperPro Designer v9.5 software (*Intelligen Inc.*, Cambridge, Massachusetts, USA) was employed to develop UF adhesive production process. In this study, five scales were analyzed: 1 t/d, 2 t/d, 5 t/d, 10 t/d and 40 t/d. The largest scale (40 t/d) has the capacity in equivalent of around 14,000 t/y. The selection of this scale is based on a commercial formaldehyde adhesive plant to be sold in *Phoenix Equipment Corporation* (plant # 271) (Phoenix Equipment Corporation, 2016). Method of performing the techno-economic analysis (TEA) is illustrated as following. The simplified overall flowchart of the UF adhesive production process is shown in Fig. 8.1.

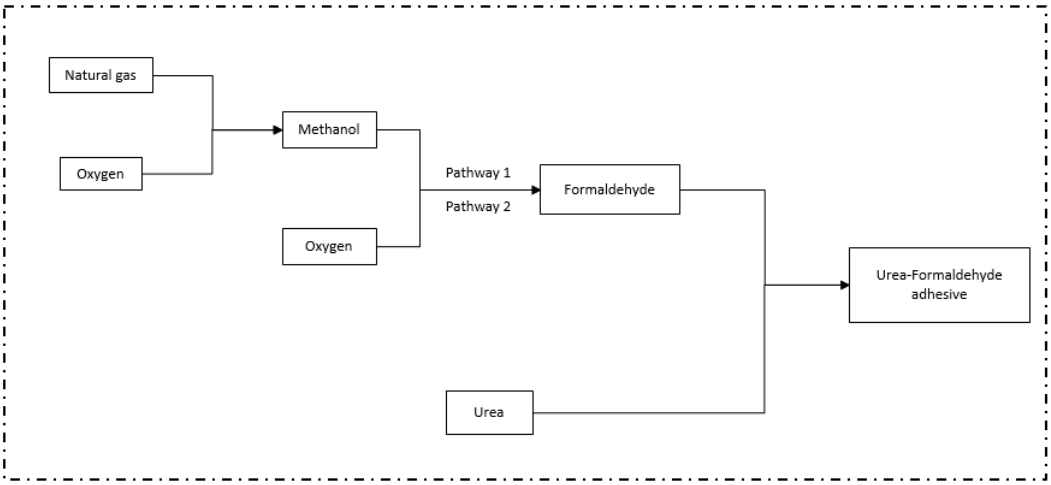

Figure 8.1 Simplified overall flowchart of UF adhesive production process.

Production process description

Formaldehyde production

In this study, two formaldehyde production processes have been studied and labeled as pathway 1 (metal oxide catalyst process) and pathway 2 (silver catalyst process).

Metal oxide catalyst process (MO process) requires lower pressures than silver catalyst pathway. The specific process is described as follows: methanol is vaporized and mixed with air in the reactor. The reactions happened in the reactor could be explained by Eq. 8.1 and Eq. 8.2 in Table 8.1. Iron (III) oxide and molybdenum trio are employed as the catalysts and the ratio of Fe/Mo is approximately 1: 4. The temperature inside the reactor is maintained at 285°C. After nitrogen and oxygen is separated from the main stream, it cools down to 110°C; and the absorption process is followed afterwards. Formic acid is separated as the co-product, and the formaldehyde is condensed as well as the methanol. The final products contain 37 wt. % formaldehyde solution and nearly 1 wt.% methanol.

As for the silver catalyst process (S process), many patents described the conventional production process (Kiser and Hendricks, 1978; Wachs and Wang, 2000). In this study, S process begins with the mixing of methanol and air, and the ratio of them is about 40%. Initial air pressure is set to be 0.2 atm. In addition, the mixture temperature is maintained at 550°C in the reactor; Eq. 3 below is the main reaction. Hydrogen is produced and separated in the following step. Then the product stream is sent to the purification and recovery section. Unreacted methanol is separated from the mainstream, approximately 18% of the input methanol. 37 wt.% formaldehyde is the final product from this process.

The computer models of these two pathways generated from SuperPro Designer are shown in Fig. 8.2 and Fig. 8.3.

UF adhesive production

Based on Taylor, the urea-formaldehyde adhesive production process starts with the blending of formaldehyde and urea at a molar ratio of 2.6:1; then water is evaporated until total water content is nearly 50 wt.%. After that, extra urea is added further to adjust the molar ratio of formaldehyde to urea to 1.5:1. Sodium hydroxide is added in this stage to adjust pH to 8-9. At the end of this stage, methylol urea is formed as Eq. 8.5 shows. Next stage is to condensate the methylol urea to low molecular weight polymers. Acid is added to bring the pH to around 5. Water is removed by distillation process in order to reach a desire solid resin content to about 65% (Taylor, 1985).

The computer model of UF adhesive production process is shown in Fig. 8.4.

Table 8.1 Reaction mechanism of UF adhesive production process (Sanhoob et al., 2012).

Number	Reaction Equations	ΔH
1	$CH_3OH + 0.5\ O_2 \rightarrow HCHO + H_2O$	- 159 kJ/mol
2	$HCHO + 0.5\ O_2 \rightarrow CO + H_2O$	- 314 kJ/mol
3	$CH_3OH \rightarrow HCHO + H_2$	+ 84 kJ/mol
4	$H_2 + 0.5O_2 \rightarrow H_2O$	- 242 kJ/mol
5	$NH_2CONH_2 + HCHO \leftrightarrow NH_2CONHCH_2OH$	- 229.9 kJ/mol

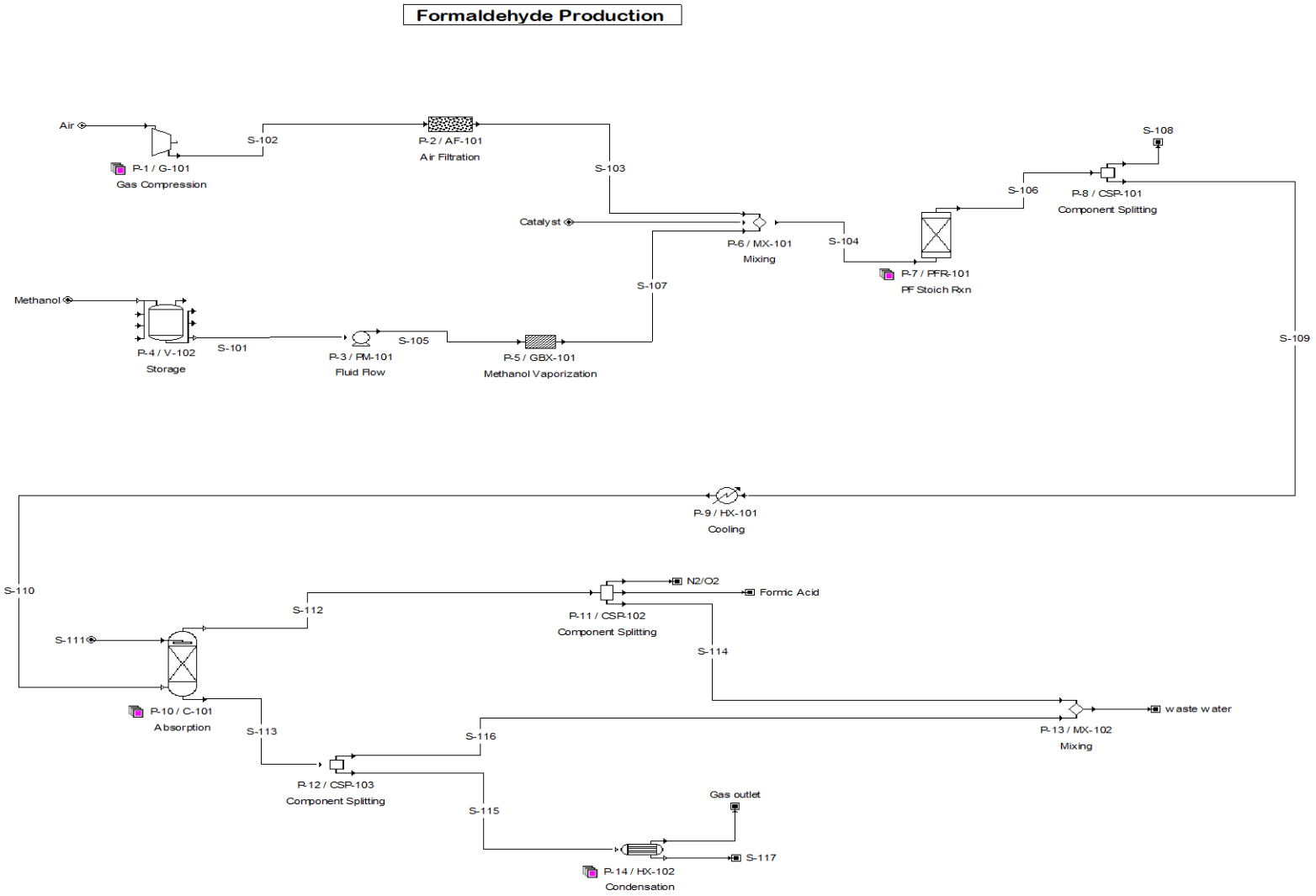

Figure 8.2 Computer model generated from SuperPro Designer software (Pathway 1: MO process).

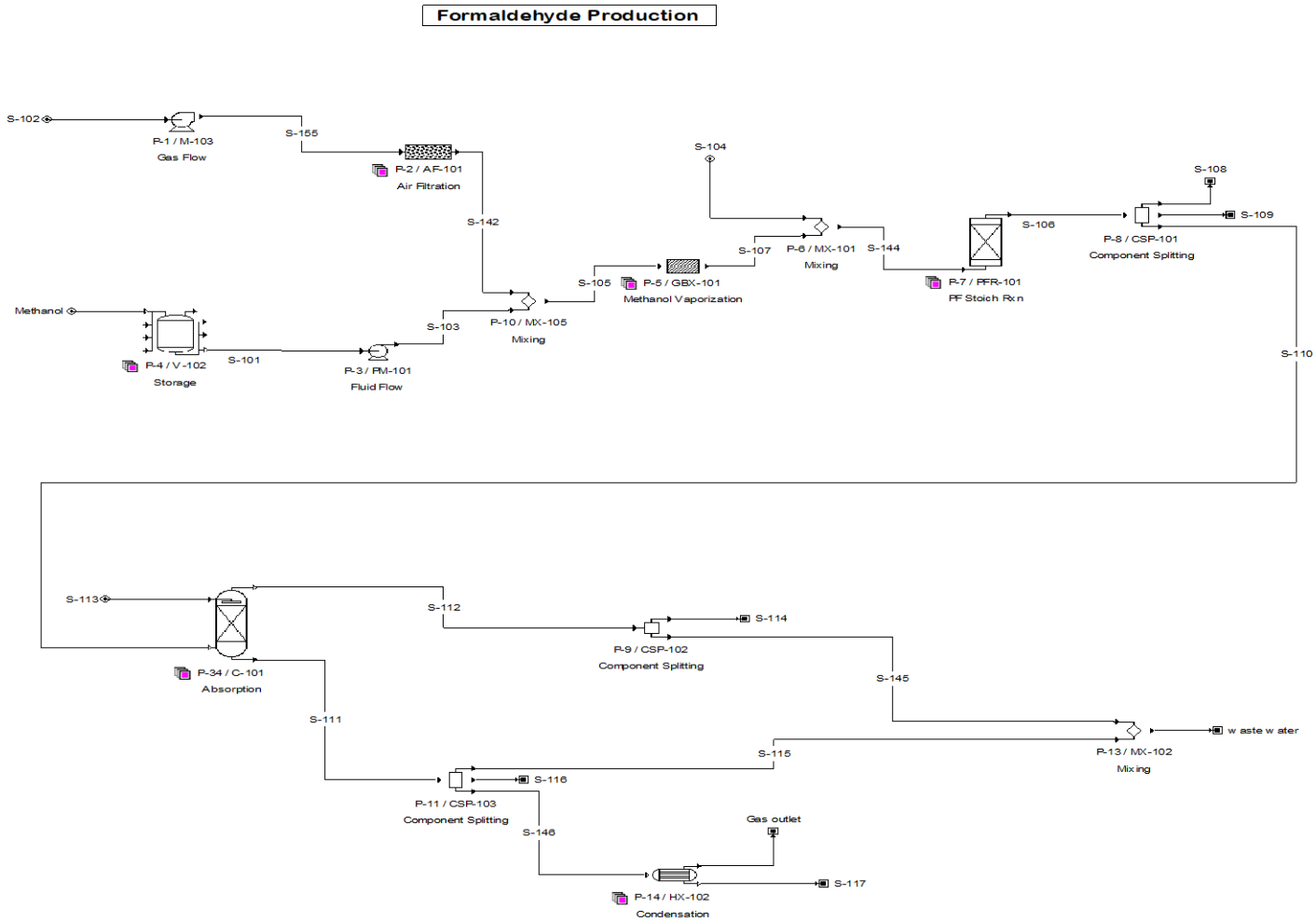

Figure 8.3 Computer model generated from SuperPro Designer (Pathway 2: S process).

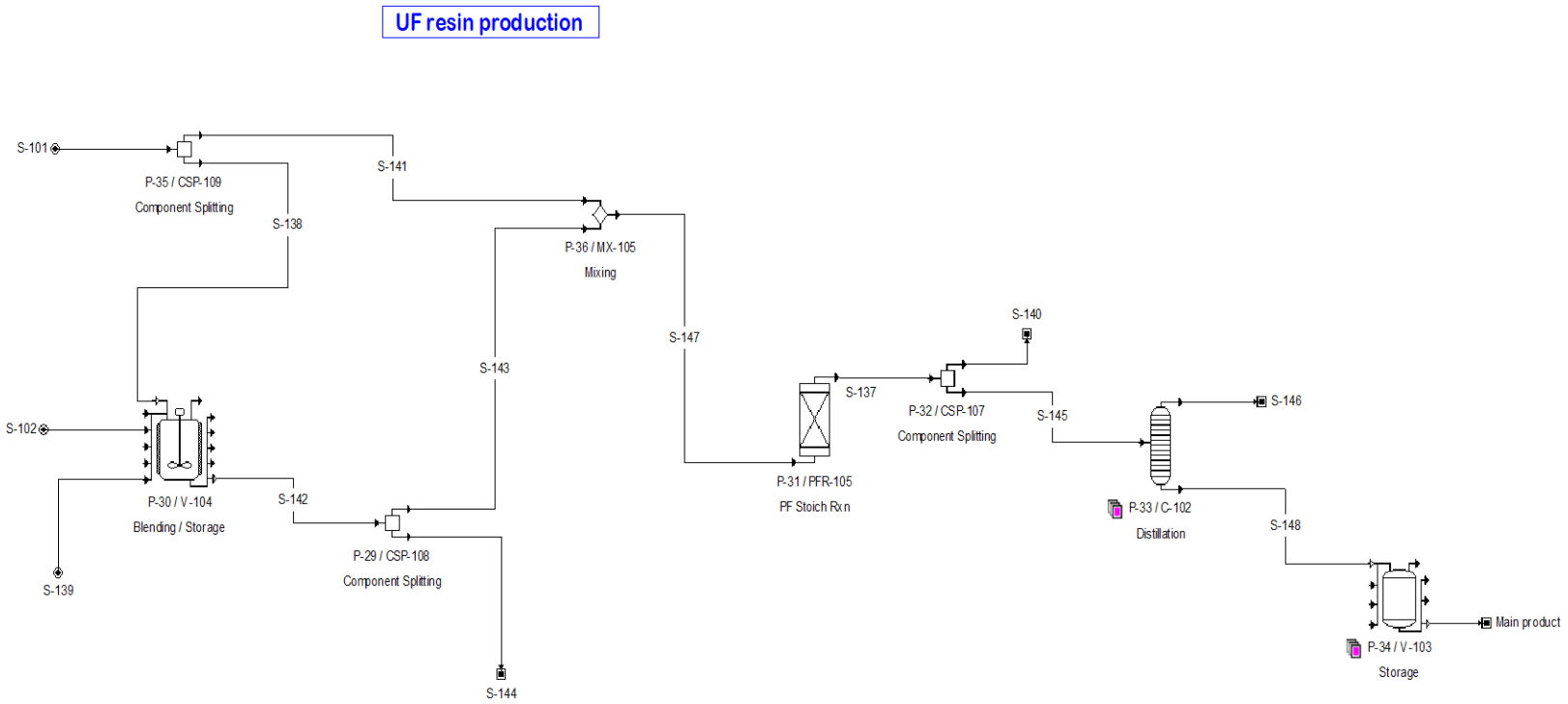

Figure 8.4 Computer model generated from SuperPro Designer (UF adhesive production process).

TEA model development

As mentioned in previous, two formaldehyde production pathways are adopted in this study. Thus, ten scenarios are considered (Table 8.2). Scenario 1-5: Metal oxide catalyst pathway (MO process) with five different scales; Scenario 6-10: Silver catalyst pathway (S process) with five different scales. Results from these scenarios will be compared based on the economic and production potential. Several economic parameters were analyzed according to the computer model characteristics.

Table 8.2 Scenarios used in UF adhesive production process.

Scenarios	Characteristics
1	Pathway 1: MO process with plant scale of 1 t/d
2	Pathway 1: MO process with plant scale of 2 t/d
3	Pathway 1: MO process with plant scale of 5 t/d
4	Pathway 1: MO process with plant scale of 10 t/d
5	Pathway 1: MO process with plant scale of 40 t/d
6	Pathway 2: S process with plant scale of 1 t/d
7	Pathway 2: S process with plant scale of 2 t/d
8	Pathway 2: S process with plant scale of 5 t/d
9	Pathway 2: S process with plant scale of 10 t/d
10	Pathway 2: S process with plant scale of 40 t/d

Total capital investment (C_{TCI})

Total capital investment (C_{TCI}) is the sum of the direct fixed costs (C_{DFC}) associated with the study, the startup and validation (C_S) cost, and the working capital (C_W) (Eq. 8.6). Assumptions of the total capital investment are listed in Table 8.3.

$$C_{TCI} = C_{DFC} + C_S + C_W \quad \text{(Eq. 8.6)}$$

Direct fixed costs (C_{DFC}) is composed of direct cost (C_{DC}), indirect cost (C_{IC}) and other cost (C_{OC}). In direct cost (C_{DC}) section, piping, instrumentation, insulation, electrical facilities, buildings, yard improvement, auxiliary facilities, installation fee are considered. The equipment purchase cost is obtained from SuperPro Designer v9.5 database, other factors associated with each cost item is taken from Peters et al. (Peters et al., 2011). Indirect cost contains engineering cost and construction cost, and other cost refers to contractor's fee and contingency fee. Working capital (C_w) is specified as the sum of major operation cost in a certain period. C_w is assumed 15% of the direct fixed cost. Start-up and validation (C_s) cost refers to the one-time pre-opening production cost. In this study, it is estimated as 10% of the direct fixed cost.

Table 8.3 Assumptions used in total capital cost investment (C_{TCI}) calculation.

Parameters	**Assumption**	**Sources**
1. Direct fixed capital cost (C_{DFC})	C_{DC} + C_{IC} + C_{OC}	
1) Direct cost (C_{DC})		
Equipment purchase cost (C_{PC})	1	SuperPro Designer v9.5 database
Piping	0.68* C_{PC}	Peters et al., 2015
Instrumentation	0.50* C_{PC}	Peters et al., 2015
Insulation	0.03* C_{PC}	Peters et al., 2015
Electrical facilities	0.30* C_{PC}	Peters et al., 2015
Building	0.45* C_{PC}	Peters et al., 2015
Yard improvement	0.20* C_{PC}	Peters et al., 2015

Table 8.3. (continued)

Parameters	Assumption	Sources
Auxiliary facilities	0.55* C_{PC}	Peters et al., 2015
Installation	0.55* C_{PC}	Peters et al., 2015
2) Indirect cost (C_{IC})		
Engineering	0.30* C_{DC}	Heinzle et al., 2015
Construction	0.35* C_{DC}	Heinzle et al., 2015
3) Other cost (C_{OC})		
Contractor's fee	0.06*(C_{DC} + C_{IC})	Peters et al., 2015
Contingency	0.08*(C_{DC} + C_{IC})	Peters et al., 2015
2. Working capital (C_W)	0.15* C_{DFC}	Ulrich, 1984
3. Start-up and validation cost (C_S)	0.10* C_{DFC}	Peters et al., 2015

Annual operating cost (C_{AOC})

The annual operating cost (C_{AOC}) includes a number of cost items, including materials cost (C_M), labor cost (C_L), utilities cost (C_U), and facility cost (C_F) (Eq. 8.7). In this study, waste treatment cost, long-term storage cost, distribution and marketing cost, research and development (R&D) cost are not considered. Major assumptions for the annual operating cost (C_{AOC}) are listed in Table 8.4.

$$C_{AOC} = C_M + C_L + C_U + C_F \quad \text{(Eq. 8.7)}$$

The material cost (C_M) is obtained from the retailer websites. Silver catalyst cost is the average price of the silver-based catalyst sold by the Sigma-Aldrich Company. Electricity price is collected from the U.S. Energy Information Agency (U.S. EIA) electricity report (EIA, 2017). Other utility costs such as steam and process water are gathered from SuperPro Designer v9.5 database. The labor cost is calculated based on the U.S. Bureau of Labor

(Bureau of Labor Statistics, 2016). In this study, the labor cost is only operating labor cost; in other words, the supervisory labor cost is not considered. The depreciation cost is calculated by the straight-line method. According to the Department of Treasury, the recovery period for the manufacture of chemicals and allied products is 9.5 years (Department of Treasury, 2017). The salvage value of the purchased equipment in this study is 0 based on the description of Turton et al. (Turton et al., 2012).

Table 8.4 Assumptions used in annual operating cost (C_{AOC}) calculation.

Parameters	**Assumption**	**Source**
1. Materials cost (C_M)		
Methanol	0.55 $/kg	Ng-Tech, 2017
Silver catalyst	3,750 $/kg	Sigma-Aldrich, 2017
Iron oxide	0.71 $/kg	Alibaba, 2017
Molybdenum oxide	15.5 $/kg	InvestmentMine, 2017
Urea	0.16 $/kg	IndexMundi, 2017
Sodium hydroxide	0.35 $/kg	Alibaba, 2017
2. Utilities cost (C_U)		
Electricity	5.08 cents/kWh	EIA, 2017
Steam	12 $/MT	SuperPro Designer v9.5
Process Water	0.05 $/MT	database
3. Labor cost (C_L)		U.S. Bureau of Labor, 2016

Table 8.4. (continued)

Parameters		Assumption	Source
4. Facility cost (C_F)			
	Maintenance	0.02* C_{PC}	Peters et al., 2015
	Depreciation	Straight-line method	Department of Treasury, 2017
		Salvage value = 0	Turton et al., 2012
	Insurance	0.01* C_{DFC}	Peters et al., 2015
	Local Tax	0.02* C_{DFC}	Peters et al., 2015

Economic analysis

Unit production cost

A unit production cost is calculated by dividing the annual total investment by annual production amount (Eq. 8.8). It is used to compare the product price in a unit-base perspective: cost per kg of raw materials or products.

$$Unit\ production\ cost\ (\$/kg) = \frac{Annual\ total\ investment}{Unit\ reference\ flow} \quad \text{(Eq. 8.8)}$$

Gross margin

Gross margin is defined as the percentage of gross profit to revenues (Eq. 8.9). It is a type of direct measure of profit. With higher gross margin, the product is more likely to have higher profit.

$$Gross\ margin\ (\%) = \frac{Revenue - Cost\ of\ Goods\ Sold}{Revenue} \times 100\% \quad \text{(Eq. 8.9)}$$

Return on investment (ROI)

Return on investment is another measurement of profit. It is used to evaluate the efficiency of investments. If a negative ROI value is obtained, then the investment may lose money.

Payback time

Payback time is the estimation of the time needed to recover the cost of an investment (Eq. 8.10). With shorter payback time, the investment tends to be more attractive.

$$Payback\ time\ (years) = \frac{Total\ investment}{Net\ profit} \quad \text{(Eq. 8.10)}$$

Sensitivity analysis

Sensitivity analysis is used to explore the key input parameters to the final product value (Saltelli et al., 2008). In this study, several input variables were selected based on the potential impact of the product value. Due to the uncertainty associated with the TEA study, the total capital investment were varied in the range between ± 30%. Other parameters such as material cost, utility cost, labor cost and product yield may have influence on the product value.

Results and Discussion

TEA result of pathway 1 (MO process)

Techno-economic analysis (TEA) results of the metal oxide catalyst pathway, aka Scenario 1-5, is listed in Table 8.5. With increasing plant capacity, the capital cost and the operating cost are increasing, and the unit cost of UF adhesive is decreasing. More specifically, as shown in Fig. 8.5, the capital cost of metal oxide catalyst pathway follows the trend line: $y = 5E+06 \times X^{0.561}$ with $R^2 = 0.97$. In addition, the unit cost of scenario 1-5 (Fig. 8.6) has the trend line: $y = 2.26 \times X^{-0.287}$ with $R^2 = 0.92$. The lowest unit cost obtained is \$0.86/kg from Scenario 5 (40 t/d).

Table 8.5 Economic analysis results (Scenario 1-5) of UF adhesive production process.

Scale (t/d)	Total capital investment ($)	Annual operating cost ($)	Unit production cost ($/kg)
1	5,896,229.63	538,328.19	2.67
2	6,009,160.16	739,961.52	1.64
5	11,541,204.68	1,537,158.06	1.32
10	19,718,523.00	2,826,576.81	1.11
40	40,065,417.56	9,820,998.64	0.86

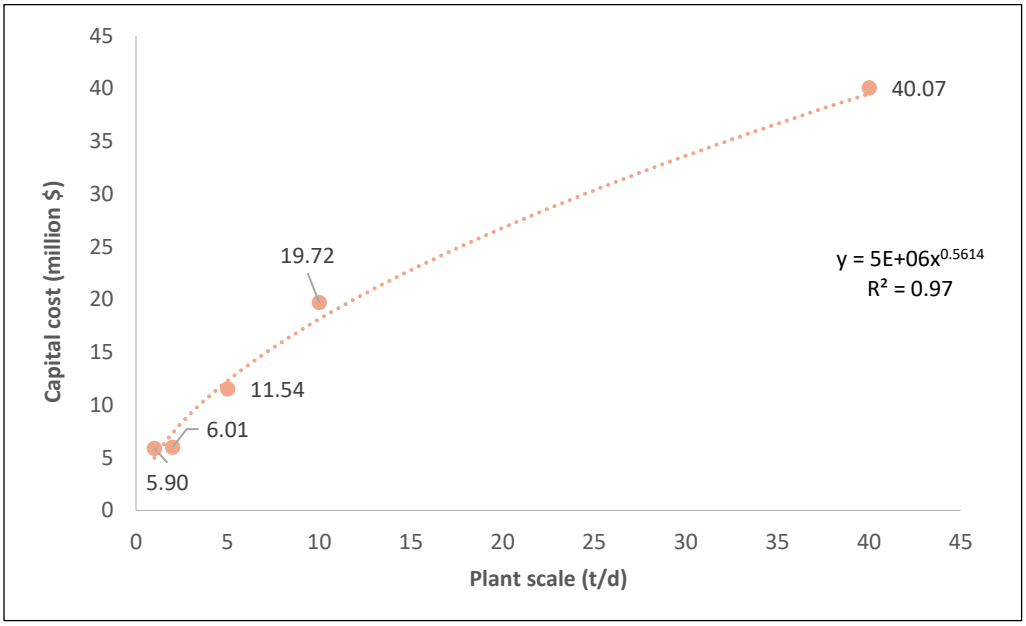

Figure 8.5 Total capital investment of the metal oxide catalyst pathway in UF adhesive production.

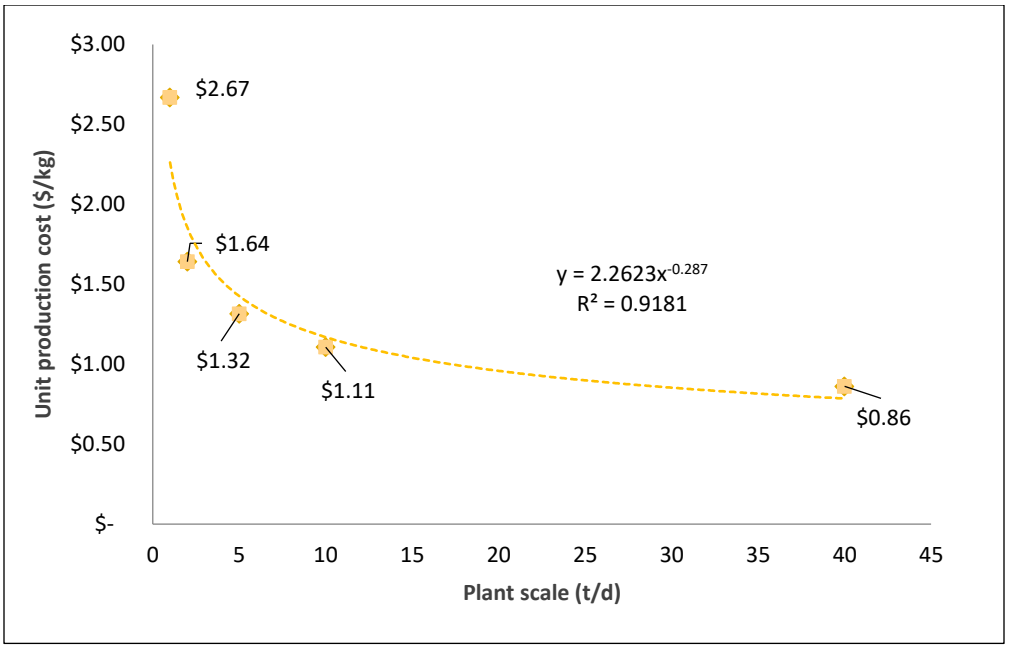

Figure 8.6 Unit production cost of the metal oxide catalyst pathway in UF adhesive production.

TEA result of pathway 2 (S process)

Table 8.6 listed the overall cost analysis results of Scenario 6-10: silver catalyst pathway. Same as metal oxide catalyst pathway, with increasing plant capacity, the capital cost and the operating cost are increasing, and the unit cost of UF resin is decreasing. The trend line of capital cost for silver catalyst pathway follows the trend line: $y = 6E+06x^{0.48}$ with $R^2= 0.99$ (Fig. 8.7). Moreover, the unit cost of scenario 6-10 (Fig. 8.8) has the trend line: $y = 2.56x^{-0.29}$ with $R^2=0.90$. The lowest unit production cost obtained is $ 1.01/kg from Scenario 10 (40 t/d).

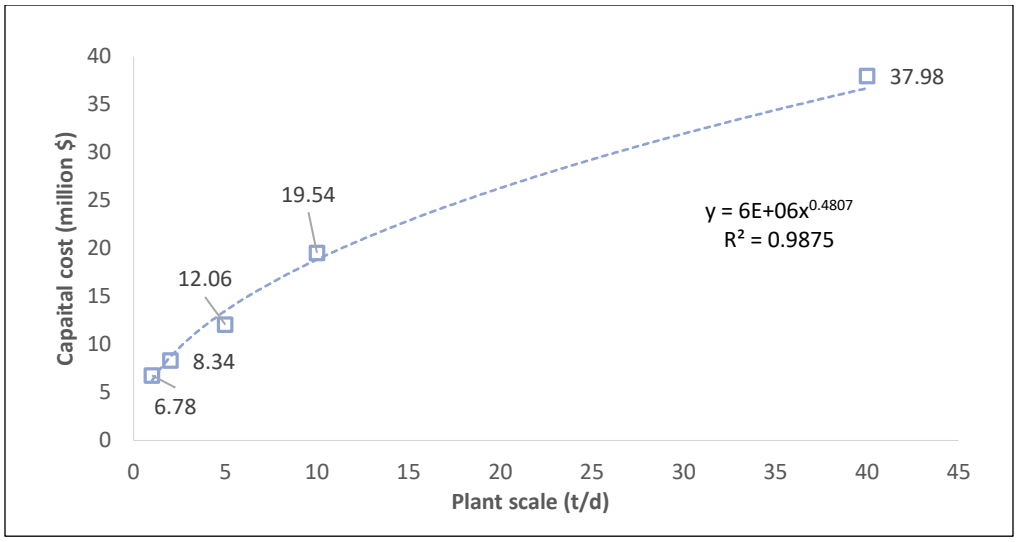

Figure 8.7 Total capital investment of the silver catalyst pathway in UF adhesive production.

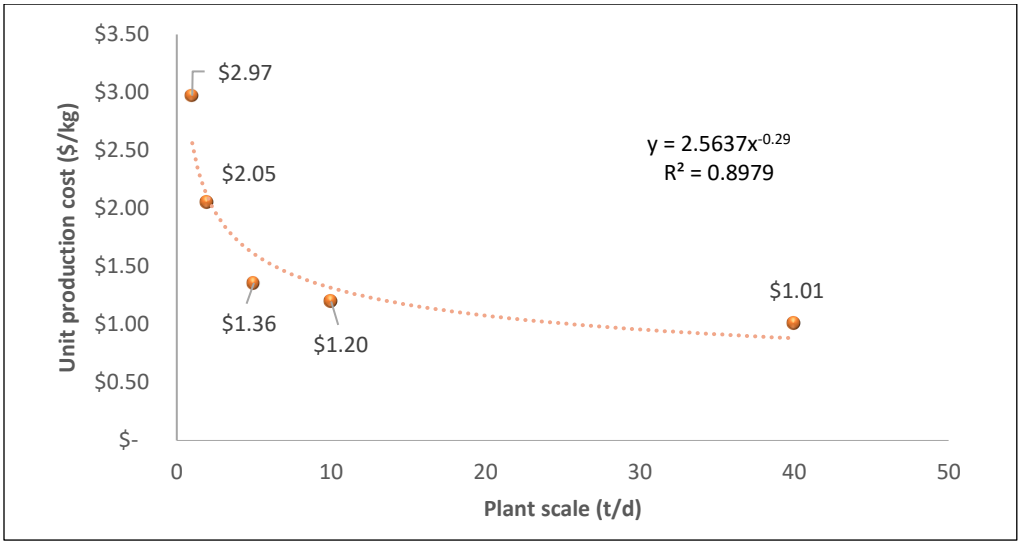

Figure 8.8 Unit production cost result of the silver catalyst pathway in UF adhesive production.

Table 8.6 Economic analysis result (Scenario 6-10) of UF adhesive production process.

Scale (t/d)	Total capital investment	Annual operating cost	Unit production cost
1	$ 6,775,738.20	$ 616,112.24	2.97 $/kg

Table 8.6. (continued)

Scale (t/d)	Total capital investment	Annual operating cost	Unit production cost
2	$ 8,336,921.18	$ 924,682.93	2.05 $/kg
5	$ 12,063,041.10	$ 1,642,794.07	1.36 $/kg
10	$ 19,544,577.53	$ 3,002,802.02	1.20 $/kg
40	$ 37,977,601.61	$ 11,998,430.62	1.01 $/kg

Total capital investment (C_{TCI}) comparison

Total capital investment (C_{TCI}) has been compared between the two largest scales: Scenario 5 and 10. C_{TCI} for these two scenarios are: 40.07 million $ and 37.98 million $. When decomposing the C_{TCI}, direct fixed capital cost required more investment in MO process than in S process (32.05 million $ vs. 30.38 million $) (Fig. 8.9). As for the working capital and startup and validation cost, they are proportional to direct fixed capital cost, thus, the cost of these two items are higher in MO process. The finding of higher total capital investment in MO process is similar to the current formaldehyde production plant.

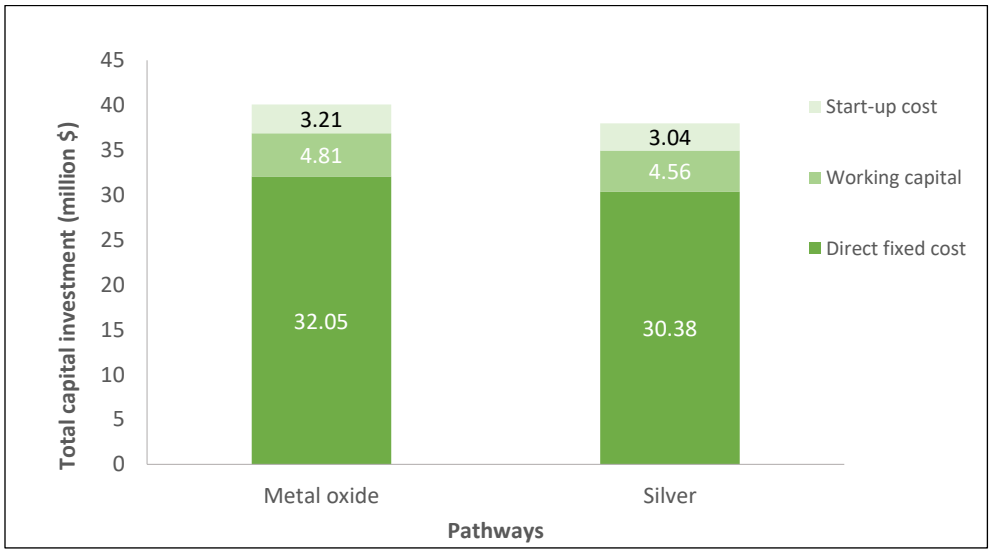

Figure 8.9 Comparison of total capital investment (C_{TCI}) between Scenario 5 and Scenario 10.

Annual operation cost (C_{AOC}) comparison

The annual operation cost (C_{AOC}) comparison for these two scenarios is shown in Fig. 8.10 below. It can be seen that S process (Scenario 10) has much higher cost than MO process (Scenario 5).

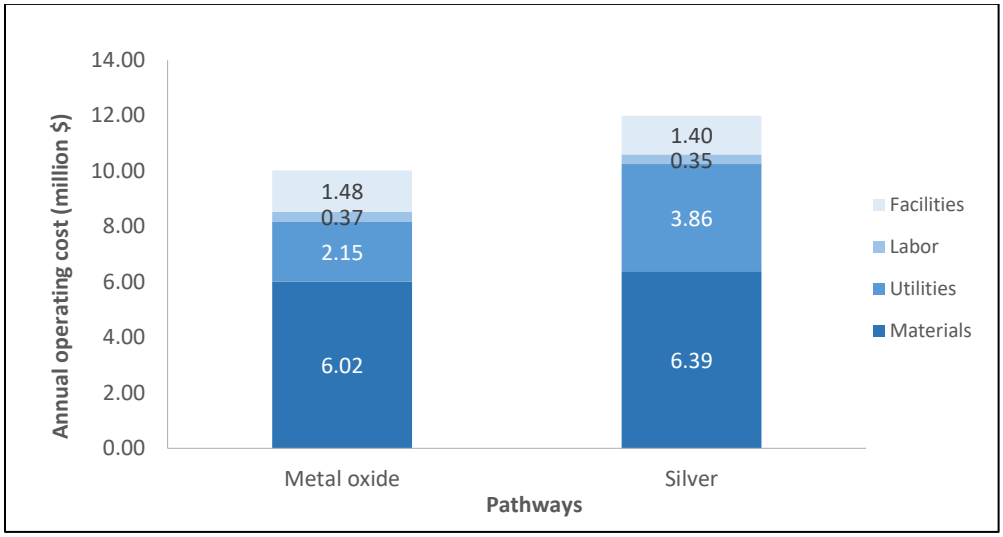

Figure 8.10 Comparison of annual operating cost (C_{AOC}) between Scenario 5 and Scenario 10.

As mentioned in previous, annual operation cost (C_{AOC}) is consist of various items, such as raw materials, utilities, labor and so on. When comparing the separate cost items in large scale (Scenario 5 vs. Scenario 10), it is observed that materials cost in Scenario 10 is much higher than that in Scenario 5, as well as the utilities cost. This could be explained by the fact that Scenario 10 employed silver as the catalyst, while Scenario 5 uses iron oxide and molybdenum oxide. Besides this, Scenario 10 requires higher temperature (around 600°C), that is where higher utilities cost as well as part of materials cost from.

Unit production cost

Unit production cost for these ten scenarios are shown in Fig. 8.11. As can be seen directly, scenario 5 has the lowest unit production cost ($0.86 /kg). By comparing with Scenario 5 and Scenario 10, silver catalyst pathway has higher unit production cost ($1.01 /kg). This result is mainly due to the higher annual operation cost.

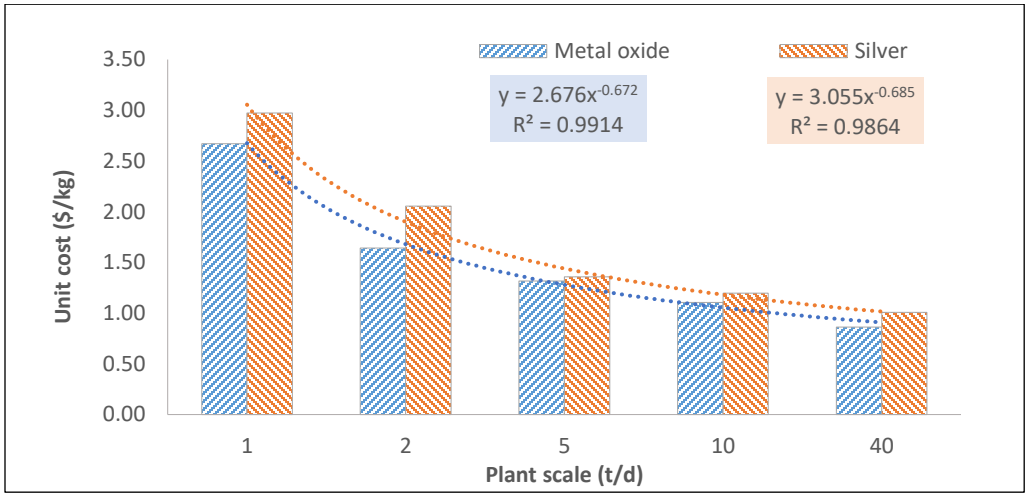

Figure 8.11 Unit production cost of the ten scenarios in UF adhesive production.

Gross margin, return on investment (ROI) and payback time

Gross margin is the difference between revenues and the cost of goods sold. As shown in Table 8.7 and Table 8.8 below, Scenario 5 has the highest gross margin (30.93%), while Scenario 6 has the lowest gross margin (-132.74%). Besides, Scenario 1, 2, 6, 7, and 8 have negative gross margin, while larger scale plants (Scenario 3, 4, 9, and 10) have positive outcome. The revenues for all scenarios is UF adhesive (50 wt. %), while the by-products are different. For Scenario 1 to 5 (MO process), formic acid is produced; for Scenario 6 to 10 (S process), carbon monoxide and carbon dioxide are formed. Due to the various selling price of the by-products, Scenario 1-5 could have higher gross margin compared with the other pathway.

In terms of ROI, Scenario 1 has the negative number. This indicates that the net profit of these scenario is negative, which means if adopting this scenario, there is possibility that no profit could be made. As for the other scenarios, Scenario 5 has the highest ROI result (10.86%), which means this scenario has the highest profit. As for the payback time, Scenario 5 required the shortest (9.57 years). Under the same plant size, Scenario 10 required 17.20 years.

Table 8.7 Gross margin, return on investment and payback time of the Scenarios 1-5.

	Scenario 1	**Scenario 2**	**Scenario 3**	**Scenario 4**	**Scenario 5**
Gross margin (%)	-57.40	-8.67	10.52	22.94	30.57
Return on investment (ROI, %)	-1.74	0.55	2.42	4.72	10.45
Payback time (years)	N/A	181.52	41.33	21.21	9.57

Table 8.8 Gross margin, return on investment and payback time of the Scenario 6-10.

	Scenario 6	**Scenario 7**	**Scenario 8**	**Scenario 9**	**Scenario 10**
Gross margin (%)	-74.99	-30.88	7.01	14.73	14.96
Return on investment (ROI, %)	-1.31	-1.11	1.96	3.35	5.81
Payback time (years)	N/A	N/A	50.98	29.89	17.20

Sensitivity analysis

Sensitivity analysis has been conducted in both Scenario 5 and Scenario 10. As illustrated in Fig. 8.12, the capital investment is the most sensitive variables among all input

variables in terms of the unit production cost. The product value results from $0.77 /kg to $0.97 /kg. Product yield and material cost are the second most sensitive factors. With 5% more yield, the price will increase by $0.04 /kg. By exploring the raw materials used in this research, it is found that the price of methanol and catalysts have impact on the product value.

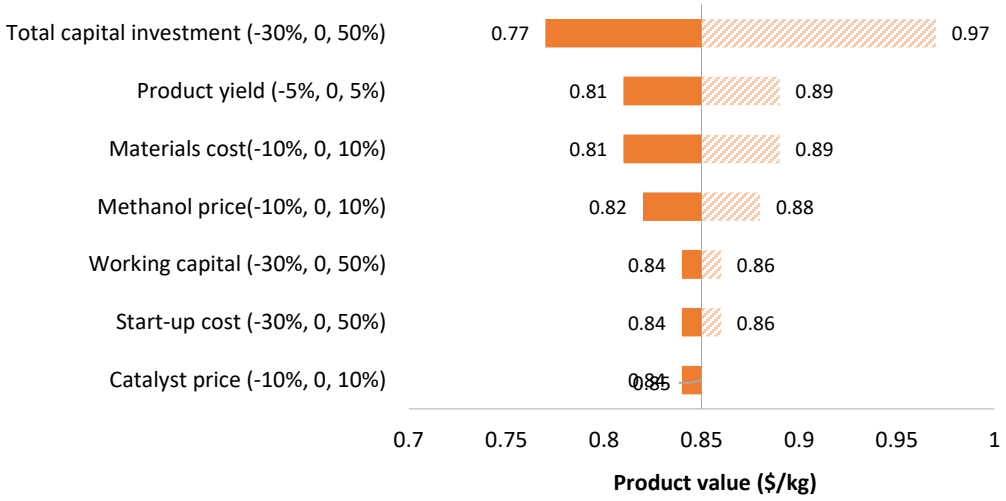

Figure 8.12 Sensitivity analysis of metal oxide catalyst pathway (Scenario 5).

As for the silver catalyst pathway (Scenario 10), total capital investment and product yield are also important factors for the unit production cost. Compared with metal oxide catalyst pathway, utility cost is the important sensitive factor for silver catalyst pathway. This is mainly due to the higher temperature requirements (around 600°C) in silver catalyst pathway.

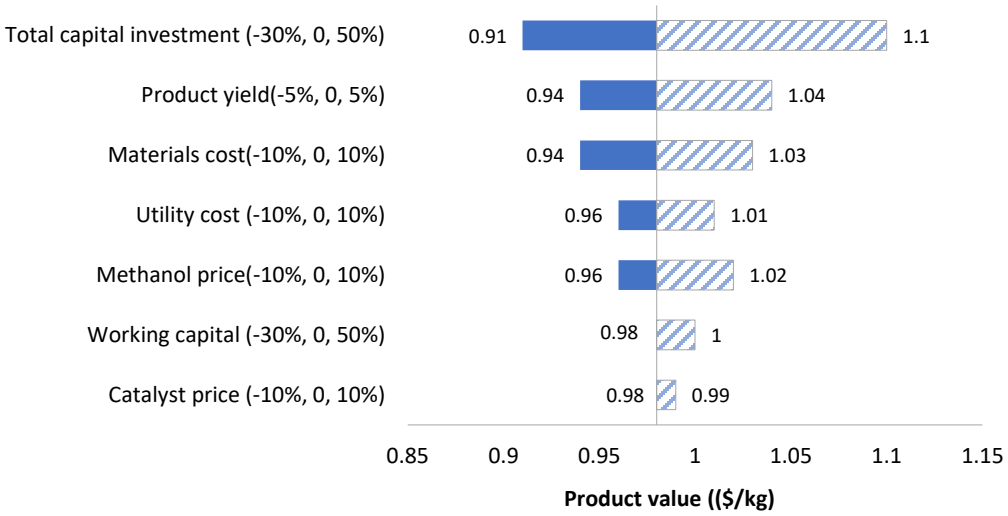

Figure 8.13 Sensitivity analysis of silver catalyst pathway (Scenario 10).

Conclusions

In this study, techno-economic analysis (TEA) of UF adhesive production process has been explored. Two pathways of formaldehyde production (metal oxide catalyst process and silver catalyst process) and five scales (from 1 t/d to 40 t/d) have been employed. Thus, ten various scenarios have been studied and compared. As a result, it is found that metal oxide catalysts pathway requires larger capital investment than silver catalyst pathway. However, the unit cost of metal oxide process is lower ($0.86 /kg) compared to silver catalyst pathway ($1.01 /kg). Based on the analysis, these two pathways are all recommended and the choice of adopting the pathway may highly depend on the initial investment.

Acknowledgements

This study was funded by the National Institute of Food and Agriculture of the United States Department of Agricultural, under the project number 214-38202-22318.

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CHAPTER 9. IMPLICATIONS

In this dissertation, the environmental impacts and economic feasibility of bio-adhesives made from the RAFT polymerization process have been explored systematically. It is essential to understand how the production of biobased materials impacts the environment in order to achieve a more sustainable future. In the meantime, the production cost of biobased adhesives highly influences the industry's choice of them, therefore, it is also necessary to investigate the cost of adhesives.

Three kinds of adhesives were chosen in this dissertation: structural adhesives, non-structural adhesives (PSA), and traditional formaldehyde-based adhesives (UF adhesive and PF adhesive). Except for traditional formaldehyde-based adhesives, the other two adhesives were produced from the RAFT polymerization process.

Environmental Performance of Adhesives from the RAFT Polymerization Process

In general, biobased adhesives have better environmental performance than petroleum-based adhesives when producing them from the RAFT polymerization process. This result is better explained by breaking down the overall impacts into specific categories, as presented in Fig. 9.1. For both structural and non-structural adhesives, resource depletion is the impact category with the largest difference (over 50%) between bio-adhesive and petro-adhesive; it contributes to nearly 50% to the overall environmental impact. Even though the weighting factor of fossil depletion used in EI-99 is less than the other two impact categories, its corresponding normalization factor is much larger as compared with others. Thus, it leads to higher contribution to the overall environmental impacts.

The differences in human health impact and ecosystem quality impact between bio-materials and petro- materials for these two adhesives are not as large as resource depletion

category. In human health impact category, bio-based PSA is around 32% less than petro-based PSA; while structural bio-adhesive is only 12% lower than structural petro-adhesive. Similar trend is observed in ecosystem quality. Bio-based PSA has 17% less impact than petro-based PSA; however, the difference between structural bio-adhesive and structural petro-adhesive is only 5%.

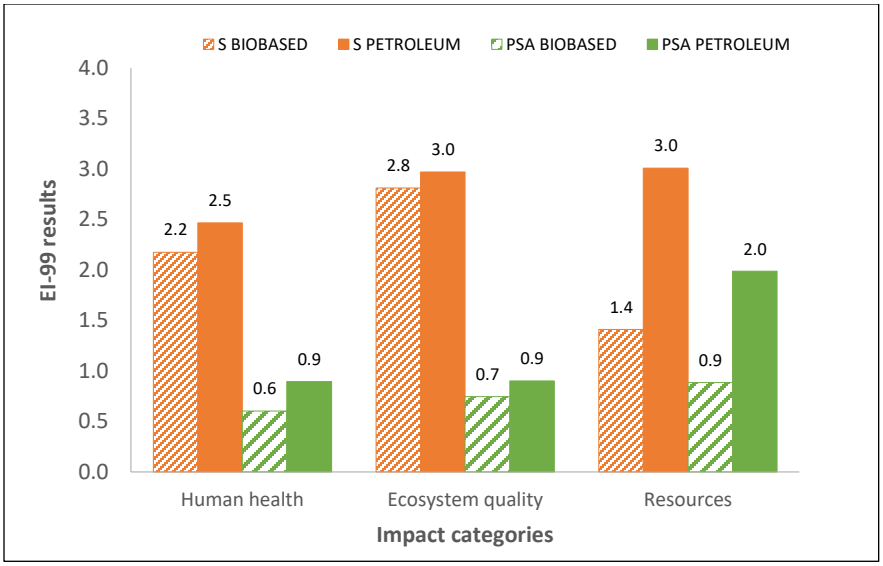

Figure 9.1 Overall environmental impact results for structural adhesive (S) and non-structural adhesive (PSA) by Eco-Indicator 99 method.

Fig. 9.2 further presents the difference between GWP results from the production of these two adhesives. For both structural adhesive and PSA, bio-based one has less emissions than petro-based. The difference between bio-based material and petro-based material in PSA is larger (37%) than that in structural adhesive (16%).

As can be observed from both overall environmental impact and the single impact category (GWP), structural adhesive seems to be less environmental friendly than PSA. The greater environmental impacts from structural adhesive can be explained by the higher molecular weight polymer (2,000,000 g/mole) required to produce it. Due to different applications, when producing PSA, the molecular weight of polymer needed is only 10,000 g/mole. Therefore, high amount of materials and energy are required for the production of structural adhesive, which lead to higher environmental impacts.

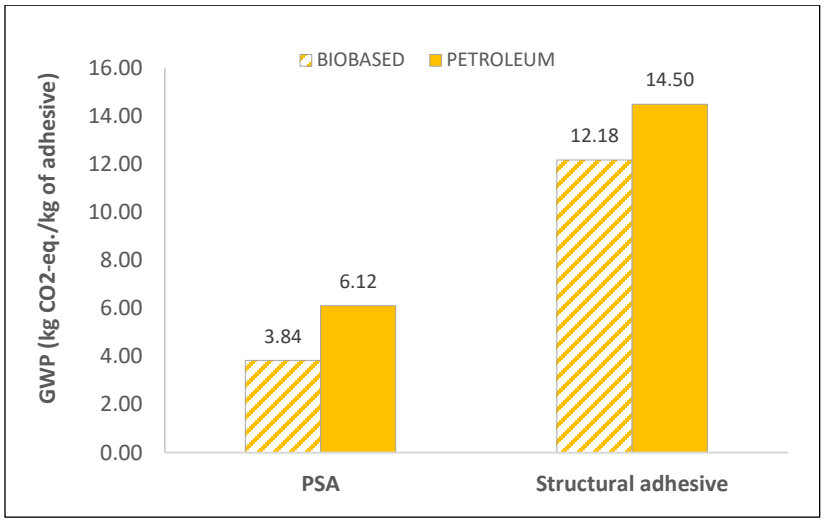

Figure 9.2 Global warming potential (GWP) results for structural adhesive and non-structural adhesive (PSA) by TRACI method.

For both structural adhesive and PSA, the RAFT polymerization process is the main contributor for GWP; while the adhesive production process itself didn't have large influence to GHG emissions. One of the methods that could significantly reduce GHG emissions is by adopting renewable sources to generate energy. Depending on the dataset from GaBi, the GHG emissions for both adhesives could be reduced by nearly 50% on average.

Environmental Performance of Structural Adhesive Compared to Traditional Formaldehyde-Based Adhesives

As formaldehyde-based adhesives are mainly used as structural adhesives, we select the structural adhesive from above to compare the environmental impacts. Fig. 9.3 shows the overall environmental performance between UF adhesive and structural bio-adhesive. The largest contributor of UF adhesive comes from human health impact. Compared with structural bio-adhesive, over 50% higher impact is observed in this impact category. As early as 1960s, the large health impact on humans from UF adhesive production process became a serious problem. Consequently, formaldehyde-free adhesives have been developed in recent decades. However, compared with structural bio-adhesive, it still has higher impacts to people.

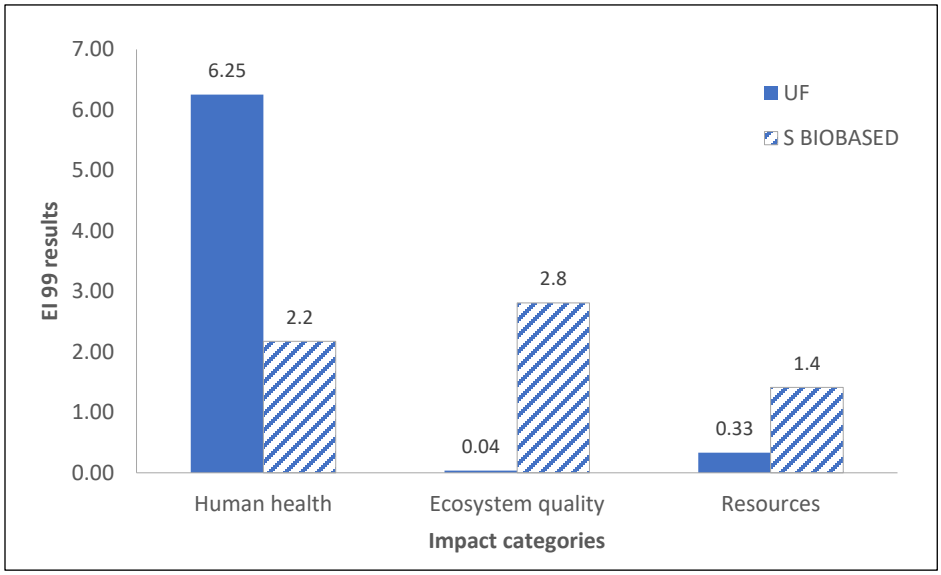

Figure 9.3 Overall environmental impact results for structural bio-adhesive (S BIOBASED) and formaldehyde-based adhesives (UF) by Eco-Indicator 99 method.

Despite higher human health impact from UF adhesive, it has much lower GWP result compared with structural bio-adhesive, as shown in Fig. 9.4. This is mainly due to the relatively complicated production process of structural bio-adhesive, which requires more

materials and energy. For UF adhesive, raw materials production is the main contributor to GHG emissions; as for structural bio-adhesive, the RAFT polymerization process contributes more in GHG emissions.

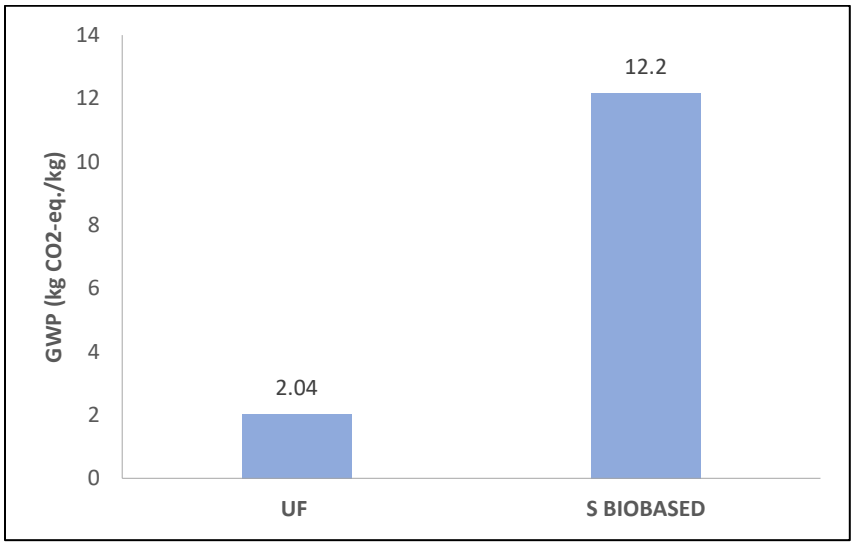

Figure 9.4 Global warming potential (GWP) results for structural bio-adhesive and UF adhesive by TRACI method.

Economic Feasibility of Structural Adhesive, PSA, and Traditional Formaldehyde-Based Adhesives

Since same plant scales were applied in all TEA studies in this dissertation, we can compare the economic indicators of these adhesives based on the same plant size. Fig. 9.5 exhibits the major TEA results of the 40 t/d production plant for these adhesives. As additional tackifier is needed in PSA production, more equipment is required to produce tackifier in the production plant. Even though a high molecular weight polymer is required in producing structural adhesive, its raw materials' price are low compared with the materials needed to produce tackifier. Therefore, higher capital investment and higher operating cost are observed in PSA production. With the same plant size and similar selling price as assumed, revenues obtained from PSA and structural adhesive are similar. Comparing with

UF adhesive, these two adhesives require larger investment in capital cost and operating cost; with the lower selling price of UF adhesive, its associated revenues are low as well. As for profit, structural adhesive has the highest result among all adhesives.

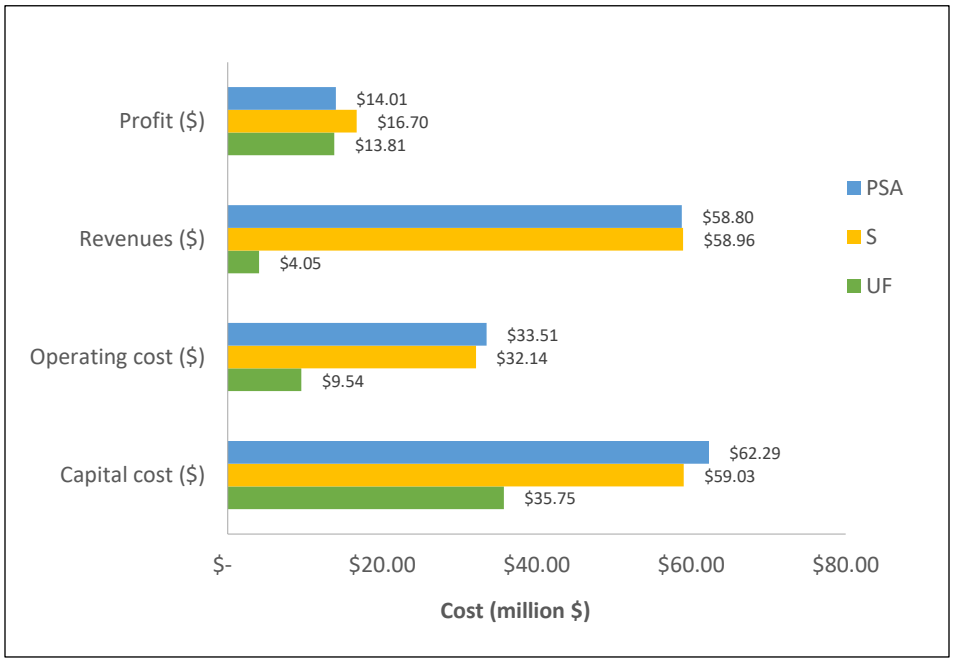

Figure 9.5 Major TEA results of the 40 t/d production plant for structural adhesive (S), PSA and UF adhesive.

Results of unit production price are shown in Fig. 9.6. Not surprisingly, UF adhesive has the lowest unit production price. Though structural adhesive has larger environmental impact than PSA, its unit production cost is lower ($2.48 /kg). The adhesive price has large influence on the market choice. Cheaper adhesives generally indicate larger market share.

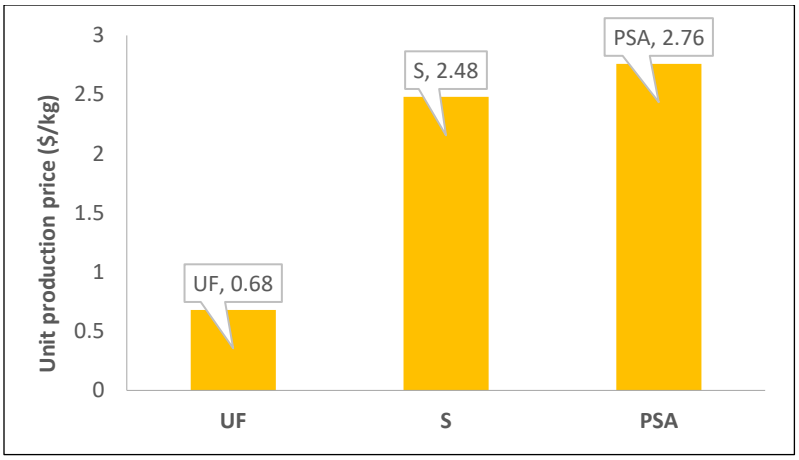

Figure 9.6 Unit production price of the 40 t/d production plant for structural adhesive, PSA and UF adhesive.

For all adhesives, raw materials cost is the one of the most sensitive parameters in terms of unit production price. By adopting petro-materials to produce adhesives, unit production price could reduce to some degree, but its associated environmental impacts may increase largely. If the current market selling price is higher than expected, it is likely that the payback time could reduce, and a lower unit production cost may be obtained.

Recommendations

Our results indicate that each adhesive has its own strength and weakness. Traditional formaldehyde-based adhesive is a low-price product with high environmental impact to humans. PSA has less environmental impact than structural adhesive, but it requires higher investment for industry production. Furthermore, bio-based adhesive is more environmental friendly than petro-based adhesive in general. However, due to different applications of the adhesives, different choices can be made based on the results from this dissertation. In order to achieve a more sustainable future, we recommend that industries should consider not only the adhesive's economic profit, but also its associated environmental impacts.

CHAPTER 10. CONCLUSIONS AND FUTURE WORK

Summary of findings

In traditional formaldehyde-based adhesive study, UF adhesive and PF adhesive were compared from environmental aspect. The results showed that UF adhesive has lower global warming impact (2.04 kg CO_2-eq/kg UF adhesive) than PF adhesive (2.88 kg CO_2-eq/kg PF adhesive), as well as overall environmental impacts. TEA study of traditional formaldehyde-based adhesive was carried out in UF adhesive due to its wider industrial applications. It was found that UF adhesive produced from metal oxide catalyst pathway has lower unit production cost as $0.86 /kg.

In structural bio-adhesive study, the structural bio-adhesive was produced from reversible addition-fragmentation chain transfer (RAFT) polymerization process. Glycerol, one of the main materials of monomer, was supplied from biodiesel plants. As a result, when producing 1 kg of structural bio-adhesive, 12.39 kg CO_2-eq emissions were observed. Compared with structural petro-adhesive, the overall environmental impact was higher than bio-adhesive. The economic analysis estimated the lowest unit production cost of the structural bio-adhesive was $2.45 /kg.

As for non-structural bio-adhesive study, pressure sensitive adhesive (PSA) was used as the final product. Glycerol was also supplied from biodiesel plant as structural adhesive, and RAFT polymerization process was employed to produce PSA. LCA results indicated that there was less evidence of GHG emissions observed in bio-adhesive than petro-adhesive. Furthermore, the unit production cost was determined to be $2.76 /kg for PSA production process.

Future work

The results from this dissertation can provide industry as well as policy maker valuable information in adhesive production system. However, LCA and TEA are still under development in fields other than biofuels. Thus, more comprehensive assessments could be conducted in the future work.

First, because of the uncertainties associated with LCA and TEA, uncertainty analysis is needed for accuracy purpose. In this dissertation, we investigated the robustness of models by sensitivity analysis and scenario analysis. In future studies, Monte Carlo simulation with random sampling could be used for uncertainty analysis. This technique could help the results become more accurate and convincing.

Secondly, the substitution of various materials and polymerization process could be investigated for further studies. This could help to reduce the unit production cost of bio-adhesive. Bio-adhesive can be more competitive to petro-adhesive in this way.

Thirdly, a more detailed comparison within structural adhesives could be investigated. As explained in Chapter 1, many adhesives can be used as structural adhesives. Each of them has unique production pathway. By conducing LCA and TEA on various structural adhesives, the results are more complete and it can help industry to make more sustainable products.

APPENDIX. PROCESS MODELED IN GABI

Table A1 Urea formaldehyde (UF) adhesive modeled in GaBi.

UF adhesive	Amount	Unit
Air [Renewable resources]	4.61E+00	kg
Antimony [Non renewable elements]	5.12E-11	kg
Barium sulphate [Non renewable resources]	2.17E-16	kg
Basalt [Non renewable resources]	4.44E-08	kg
Bauxite [Non renewable resources]	3.46E-05	kg
Bentonite [Non renewable resources]	8.59E-04	kg
Biotic Production [Occupation]	7.30E-03	kg
Biotic Production [Transformation]	5.43E-06	kg/a
Calcium chloride [Non renewable resources]	2.22E-14	kg
Carbon dioxide [Renewable resources]	3.08E-02	kg
Chromium [Non renewable elements]	1.72E-06	kg
Clay [Non renewable resources]	1.75E-04	kg
Coalbed methane (in MJ) [Natural gas (resource)]	4.25E-01	MJ
Cobalt [Non renewable elements]	2.12E-11	kg
Colemanite ore [Non renewable resources]	4.01E-07	kg
Copper [Non renewable elements]	1.32E-05	kg
Crude oil (in kg) [Crude oil (resource)]	7.27E-04	kg
Crude oil (in MJ) [Crude oil (resource)]	3.43E-01	MJ
Diesel [Refinery products]	3.43E-03	kg
Dolomite [Non renewable resources]	4.39E-05	kg
Electricity (product) [Electric power]	2.40E-01	MJ
Electricity [Electric power]	5.85E-01	MJ
Erosion Resistance [Occupation]	7.36E-04	kg
Erosion Resistance [Transformation]	4.32E-08	kg/a
Feldspar (aluminium silicates) [Non renewable resources]	2.98E-21	kg
Ferro manganese [Non renewable resources]	4.51E-17	kg
Fluorspar (calcium fluoride; fluorite) [Non renewable resources]	1.25E-06	kg
Formaldehyde (37%; methanol) [Organic intermediate products]	1.49E+00	kg
Formic acid [Organic intermediate products]	1.01E-03	kg
Gasoline (regular) [Refinery products]	1.71E-04	kg
Gold [Non renewable elements]	9.37E-11	kg
Granite [Non renewable resources]	2.99E-21	kg
Graphite [Non renewable resources]	8.15E-11	kg
Groundwater Replenishment [Transformation]	1.14E-03	(mm*m2)/a
Gypsum (natural gypsum) [Non renewable resources]	5.52E-05	kg
Hard coal (in MJ) [Hard coal (resource)]	3.43E-01	MJ
Hard coal USA [Hard coal at production]	1.71E-01	kg

Table A1. (continued)

UF adhesive	Amount	Unit
Heavy spar (BaSO4) [Non renewable resources]	1.58E-08	kg
Ilmenite (titanium ore) [Non renewable resources]	7.46E-08	kg
Inert rock [Non renewable resources]	5.75E-01	kg
Iridium [Non renewable elements]	3.93E-14	kg
Iron [Non renewable elements]	1.42E-03	kg
Kaolin ore [Non renewable resources]	2.25E-08	kg
Land Occupation [Occupation]	1.04E-02	m2*yr
Land Transformation [Transformation]	1.04E-02	sqm
Lead [Non renewable elements]	2.52E-05	kg
Lignite (in MJ) [Lignite (resource)]	4.08E-01	MJ
Limestone (calcium carbonate) [Non renewable resources]	5.32E-03	kg
Magnesit (Magnesium carbonate) [Non renewable resources]	4.56E-06	kg
Magnesium [Non renewable elements]	5.30E-08	kg
Magnesium chloride leach (40%) [Non renewable resources]	7.41E-05	kg
Manganese [Non renewable elements]	1.86E-05	kg
Mechanical Filtration [Occupation]	4.46E+00	cm*m²
Mercury [Non renewable elements]	1.40E-16	kg
Molybdenum [Non renewable elements]	2.14E-07	kg
Natural Aggregate [Non renewable resources]	2.52E-02	kg
Natural gas (in MJ) [Natural gas (resource)]	9.29E+00	MJ
Natural gas USA [Natural gas (resource)]	1.10E+00	kg
Natural pumice [Non renewable resources]	3.52E-07	kg
Nickel [Non renewable elements]	6.84E-08	kg
Nitrogen [Renewable resources]	4.42E-12	kg
Occup. as Convent. arable land [Hemeroby]	4.00E-03	m2*yr
Oil sand (10% bitumen) (in MJ) [Crude oil (resource)]	8.56E-03	MJ
Oil sand (100% bitumen) (in MJ) [Crude oil (resource)]	7.48E-03	MJ
Olivine [Non renewable resources]	4.78E-16	kg
Osmium [Non renewable elements]	4.79E-14	kg
Oxygen [Renewable resources]	4.37E-04	kg
Palladium [Non renewable elements]	6.95E-13	kg
Peat (in MJ) [Peat (resource)]	5.01E-05	MJ
Phosphate ore [Non renewable resources]	1.12E-05	kg
Phosphorus [Non renewable elements]	9.56E-07	kg
Physicochemical Filtration [Occupation]	5.97E-03	(cmol*m2*a)/kg
Pit Methane (in MJ) [Natural gas (resource)]	5.34E-03	MJ
Platinum [Non renewable elements]	1.17E-12	kg
Potashsalt crude (hard salt 10% K2O) [Non renewable resources]	6.71E-04	kg
Potassium chloride [Non renewable resources]	2.29E-13	kg
Primary energy from geothermics [Renewable energy resources]	9.15E-05	MJ
Primary energy from hydro power [Renewable energy resources]	3.42E-01	MJ

Table A1. (continued)

UF adhesive	Amount	Unit
Primary energy from solar energy [Renewable energy resources]	3.19E-01	MJ
Primary energy from waves [Renewable energy resources]	3.10E-13	MJ
Primary energy from wind power [Renewable energy resources]	1.21E-01	MJ
Primary forest [Renewable resources]	1.80E-12	kg
Pyrite [Non renewable resources]	3.55E-07	kg
Quartz sand (silica sand; silicon dioxide) [Non renewable resources]	4.05E-04	kg
Rhodium [Non renewable elements]	1.17E-13	kg
RNA: Dummy_Electricity at wind power plant unspecified [Dummy Flows]	1.93E-01	MJ
Ruthenium [Non renewable elements]	2.33E-13	kg
Shale [Non renewable resources]	2.06E-06	kg
Shale gas (in MJ) [Natural gas (resource)]	1.86E+00	MJ
Silicon [Non renewable elements]	5.80E-08	kg
Silver [Non renewable elements]	3.28E-08	kg
Sodium chloride (rock salt) [Non renewable resources]	3.62E-03	kg
Sodium hydroxide (100%; caustic soda) [Inorganic intermediate products]	1.89E-03	kg
Sodium nitrate [Non renewable resources]	1.52E-26	kg
Sodium sulphate [Non renewable resources]	5.20E-15	kg
Soil [Non renewable resources]	2.35E-02	kg
Stone from mountains [Non renewable resources]	1.30E-04	kg
Sulphur [Non renewable elements]	1.83E-05	kg
Talc [Non renewable resources]	6.19E-10	kg
Tantalum [Non renewable elements]	2.60E-10	kg
Tight gas (in MJ) [Natural gas (resource)]	1.63E+00	MJ
Tin [Non renewable elements]	6.80E-20	kg
Tin ore [Non renewable resources]	9.40E-08	kg
Titanium [Non renewable elements]	2.98E-09	kg
Titanium ore [Non renewable resources]	1.81E-09	kg
Uranium natural (in MJ) [Uranium (resource)]	2.92E-01	MJ
Uranium oxide (U3O8) 332 GJ per kg in ore [Uranium (resource)]	4.71E-07	kg
Urea (agrarian) [Agro chemicals]	2.77E+00	kg
US: Dummy_Disposal ash and flue gas desulfurization sludge to unspecified reuse [Dummy Flows]	3.17E-03	kg
US: Dummy_Disposal solid waste unspecified to sanitary landfill [Dummy Flows]	4.70E-04	kg
US: Dummy_Disposal solid waste unspecified to unspecified landfill [Dummy Flows]	1.58E-04	kg
US: Dummy_Disposal solid waste unspecified to unspecified treatment [Dummy Flows]	3.37E-02	kg
US: Dummy_Electricity geothermal unspecified [Dummy Flows]	1.54E-02	MJ
US: Dummy_Transport pipeline coal slurry [Dummy Flows]	4.98E-01	kgkm
US: Dummy_Transport pipeline natural gas [Dummy Flows]	6.63E+02	kgkm

Table A1. (continued)

UF adhesive	Amount	Unit
US: Dummy_Transport pipeline unspecified [Dummy Flows]	3.05E+02	kgkm
US: electricity production mix photovoltaic at plant [power plants]	2.73E-02	MJ
US: Liquefied petroleum gas at refinery [Products and Intermediates]	7.39E-12	m3
US: Residual fuel oil combusted in industrial boiler [Products and Intermediates]	6.94E-07	m3
US: Transport barge average fuel mix [Products and Intermediates]	1.26E+01	kgkm
US: Transport combination truck average fuel mix [Products and Intermediates]	2.53E+01	kgkm
US: Transport combination truck diesel powered [Products and Intermediates]	3.90E+00	kgkm
US: Transport ocean freighter average fuel mix [Products and Intermediates]	3.33E+00	kgkm
US: Transport ocean freighter diesel powered [Products and Intermediates]	3.40E-04	kgkm
US: Transport ocean freighter residual fuel oil powered [Products and Intermediates]	3.06E-03	kgkm
US: Transport train diesel powered [Products and Intermediates]	1.08E+02	kgkm
Vanadium [Non renewable elements]	1.38E-08	kg
Water (ground water) [Water]	1.56E+00	kg
Water (lake water) [Water]	7.83E+01	kg
Water (rain water) [Water]	1.10E+00	kg
Water (river water) [Water]	5.09E+02	kg
Water (sea water) [Water]	2.64E-01	kg
Zinc [Non renewable elements]	2.03E-05	kg
Zirconium [Non renewable elements]	2.70E-14	kg

Table A2 Phenol formaldehyde (PF) adhesive modeled in GaBi.

PF adhesive	Amount	Unit
Air [Renewable resources]	1.51E+01	kg
Antimony [Non renewable elements]	1.24E-10	kg
Barium sulphate [Non renewable resources]	2.57E-15	kg
Basalt [Non renewable resources]	1.14E-07	kg
Bauxite [Non renewable resources]	9.21E-05	kg
Bentonite [Non renewable resources]	2.09E-03	kg
Biotic Production [Occupation]	1.78E-02	kg
Biotic Production [Transformation]	1.12E-05	kg/a
Calcium chloride [Non renewable resources]	2.63E-13	kg
Carbon dioxide [Renewable resources]	5.56E-02	kg
Chromium [Non renewable elements]	2.40E-06	kg
Clay [Non renewable resources]	4.15E-04	kg
Coalbed methane (in MJ) [Natural gas (resource)]	6.67E-04	MJ
Cobalt [Non renewable elements]	4.87E-11	kg
Colemanite ore [Non renewable resources]	9.88E-07	kg
Copper [Non renewable elements]	2.36E-05	kg
Crude oil (in kg) [Crude oil (resource)]	8.73E-04	kg
Crude oil (in MJ) [Crude oil (resource)]	4.11E+01	MJ
Diesel [Refinery products]	3.43E-03	kg
Dolomite [Non renewable resources]	1.09E-04	kg
Electricity (product) [Electric power]	0.272981	MJ
Electricity [Electric power]	0.143674	MJ
Erosion Resistance [Occupation]	1.53E-03	kg
Feldspar (aluminium silicates) [Non renewable resources]	7.47E-21	kg
Ferro manganese [Non renewable resources]	1.13E-16	kg
Fluorspar (calcium fluoride; fluorite) [Non renewable resources]	3.41E-06	kg
Formaldehyde (37%; methanal) [Organic intermediate products]	1.79E+00	kg
Gold [Non renewable elements]	2.33E-10	kg
Granite [Non renewable resources]	7.48E-21	kg
Graphite [Non renewable resources]	2.07E-10	kg
Groundwater Replenishment [Transformation]	2.32E-03	(mm*m2)/a
Gypsum (natural gypsum) [Non renewable resources]	1.01E-04	kg
Hard coal (in MJ) [Hard coal (resource)]	1.88E+00	MJ
Hard coal USA [Hard coal, at production]	1.52E-01	kg
Heavy spar (BaSO4) [Non renewable resources]	1.67E-07	kg
Ilmenite (titanium ore) [Non renewable resources]	1.66E-07	kg
Inert rock [Non renewable resources]	1.95E+00	kg
Iridium [Non renewable elements]	9.03E-14	kg
Iron [Non renewable elements]	1.28E-03	kg
Kaolin ore [Non renewable resources]	5.94E-08	kg

Table A2. (continued)

PF adhesive	Amount	Unit
Land Occupation [Occupation]	4.75E-02	m2*yr
Land Transformation [Transformation]	4.75E-02	sqm
Lead [Non renewable elements]	2.35E-05	kg
Lignite (in MJ) [Lignite (resource)]	1.04E+00	MJ
Limestone (calcium carbonate) [Non renewable resources]	1.55E-02	kg
Magnesit (Magnesium carbonate) [Non renewable resources]	1.34E-05	kg
Magnesium [Non renewable elements]	1.43E-06	kg
Magnesium chloride leach (40%) [Non renewable resources]	2.20E-04	kg
Manganese [Non renewable elements]	2.50E-05	kg
Mechanical Filtration [Occupation]	1.08E+01	cm*m²
Mercury [Non renewable elements]	3.51E-16	kg
Molybdenum [Non renewable elements]	3.31E-07	kg
Natural Aggregate [Non renewable resources]	4.96E-03	kg
Natural gas (in MJ) [Natural gas (resource)]	2.90E+01	MJ
Natural gas USA [Natural gas (resource)]	8.66E-01	kg
Natural pumice [Non renewable resources]	6.70E-07	kg
Nickel [Non renewable elements]	2.48E-07	kg
Nitrogen [Renewable resources]	1.11E-11	kg
Occup. as Convent. arable land [Hemeroby]	9.30E-03	m2*yr
Oil sand (10% bitumen) (in MJ) [Crude oil (resource)]	7.52E-03	MJ
Oil sand (100% bitumen) (in MJ) [Crude oil (resource)]	6.57E-03	MJ
Olivine [Non renewable resources]	1.30E-15	kg
Osmium [Non renewable elements]	1.10E-13	kg
Oxygen [Renewable resources]	1.22E-04	kg
Palladium [Non renewable elements]	1.60E-12	kg
Peat (in MJ) [Peat (resource)]	6.86E-04	MJ
Phenol (hydroxy benzene) [Organic intermediate products]	2.47E+00	kg
Phosphorus [Non renewable elements]	2.40E-06	kg
Physicochemical Filtration [Occupation]	1.49E-02	(cmol*m2*a)/kg
Pit Methane (in MJ) [Natural gas (resource)]	1.87E-02	MJ
Platinum [Non renewable elements]	2.71E-12	kg
Potashsalt, crude (hard salt, 10% K2O) [Non renewable resources]	1.18E-03	kg
Potassium chloride [Non renewable resources]	7.17E-13	kg
Primary energy from geothermics [Renewable energy resources]	1.08E-03	MJ
Primary energy from hydro power [Renewable energy resources]	3.38E-01	MJ
Primary energy from solar energy [Renewable energy resources]	8.02E-01	MJ
Primary energy from waves [Renewable energy resources]	7.77E-13	MJ
Primary energy from wind power [Renewable energy resources]	3.10E-01	MJ
Primary forest [Renewable resources]	4.51E-12	kg
Pyrite [Non renewable resources]	2.98E-07	kg

Table A2. (continued)

PF adhesive	Amount	Unit
Quartz sand (silica sand; silicon dioxide) [Non renewable resources]	2.38E-03	kg
Rhodium [Non renewable elements]	2.71E-13	kg
RNA: Dummy_Electricity, at wind power plant, unspecified [Dummy Flows]	1.29E-01	MJ
Ruthenium [Non renewable elements]	5.34E-13	kg
Shale [Non renewable resources]	4.11E-06	kg
Shale gas (in MJ) [Natural gas (resource)]	1.78E-03	MJ
Silicon [Non renewable elements]	1.58E-06	kg
Silver [Non renewable elements]	4.04E-08	kg
Sodium chloride (rock salt) [Non renewable resources]	3.05E-02	kg
Sodium nitrate [Non renewable resources]	6.64E-26	kg
Sodium sulphate [Non renewable resources]	6.16E-14	kg
Soil [Non renewable resources]	6.71E-03	kg
Stone from mountains [Non renewable resources]	1.10E-03	kg
Sulphur [Non renewable elements]	4.51E-05	kg
Talc [Non renewable resources]	1.50E-09	kg
Tantalum [Non renewable elements]	6.63E-10	kg
Tight gas (in MJ) [Natural gas (resource)]	2.41E-03	MJ
Tin [Non renewable elements]	8.09E-19	kg
Tin ore [Non renewable resources]	2.35E-07	kg
Titanium [Non renewable elements]	9.58E-09	kg
Titanium ore [Non renewable resources]	4.53E-09	kg
Uranium natural (in MJ) [Uranium (resource)]	8.16E-01	MJ
Uranium oxide (U_3O_8), 332 GJ per kg, in ore [Uranium (resource)]	3.13E-07	kg
US: Dummy_Disposal, ash and flue gas desulfurization sludge, to unspecified reuse [Dummy Flows]	2.12E-03	kg
US: Dummy_Disposal, solid waste, unspecified, to sanitary landfill [Dummy Flows]	5.64E-04	kg
US: Dummy_Disposal, solid waste, unspecified, to unspecified treatment [Dummy Flows]	2.54E-02	kg
US: Dummy_Electricity, geothermal, unspecified [Dummy Flows]	1.03E-02	MJ
US: Dummy_Transport, pipeline, coal slurry [Dummy Flows]	3.32E-01	kgkm
US: Dummy_Transport, pipeline, natural gas [Dummy Flows]	388.1419	kgkm
US: Dummy_Transport, pipeline, unspecified [Dummy Flows]	1.79E+02	kgkm
US: electricity, production mix photovoltaic, at plant [power plants]	1.82E-02	MJ
US: Liquefied petroleum gas, at refinery [Products and Intermediates]	4.82E-12	m3
US: Residual fuel oil, combusted in industrial boiler [Products and Intermediates]	5.11E-07	m3
US: Transport, barge, average fuel mix [Products and Intermediates]	8.40E+00	kgkm
US: Transport, combination truck, average fuel mix [Products and Intermediates]	3.01E+01	kgkm
US: Transport, combination truck, diesel powered [Products and Intermediates]	4.33E+00	kgkm

Table A2. (continued)

PF adhesive	Amount	Unit
US: Transport, ocean freighter, average fuel mix [Products and Intermediates]	4.00E+00	kgkm
US: Transport, ocean freighter, diesel powered [Products and Intermediates]	2.27E-04	kgkm
US: Transport, ocean freighter, residual fuel oil powered [Products and Intermediates]	2.04E-03	kgkm
US: Transport, train, diesel powered [Products and Intermediates]	7.48E+01	kgkm
Vanadium [Non renewable elements]	3.45E-08	kg
Water (ground water) [Water]	1.06E+01	kg
Water (lake water) [Water]	6.42E+01	kg
Water (rain water) [Water]	2.38E+00	kg
Water (river water) [Water]	8.79E+02	kg
Water (sea water) [Water]	9.25E-01	kg
Zinc [Non renewable elements]	2.52E-05	kg
Zirconium [Non renewable elements]	6.78E-14	kg
Vanadium [Non renewable elements]	3.45E-08	kg

Table A3 Structural bio-adhesive modeled in GaBi.

Structural bio-adhesive	Amount	Unit
AIBN [Organic intermediate products]	2.00E-02	kg
Air [Renewable resources]	2.93E+01	kg
Antimony [Non renewable elements]	3.63E-10	kg
Barium sulphate [Non renewable resources]	2.46E-15	kg
Basalt [Non renewable resources]	1.16E-07	kg
Bauxite [Inorganic intermediate products]	1.19E-01	kg
Bauxite [Non renewable resources]	1.14E-04	kg
Bentonite [Non renewable resources]	1.73E-03	kg
Biomass (solid) [Biomass fuels]	6.00E-05	kg
Biotic Production [Occupation]	2.04E-02	kg
Biotic Production [Transformation]	1.68E-04	kg/a
Calcium chloride [Non renewable resources]	2.52E-13	kg
Carbon dioxide [Renewable resources]	4.90E-01	kg
Carcass meal [Hazardous waste for recovery]	4.19E-13	kg
Chromium [Non renewable elements]	4.30E-05	kg
Clay [Non renewable resources]	1.20E-03	kg
Coalbed methane (in MJ) [Natural gas (resource)]	5.51E-01	MJ
Cobalt [Non renewable elements]	1.48E-10	kg
Colemanite ore [Non renewable resources]	1.16E-06	kg
Copper [Non renewable elements]	1.63E-04	kg
Crude oil (in kg) [Crude oil (resource)]	1.45E-01	kg
Crude oil (in MJ) [Crude oil (resource)]	1.61E+01	MJ
Diesel [Refinery products]	1.67E-01	kg
Dolomite [Non renewable resources]	1.39E-04	kg
Electricity [Electric power]	6.14E-01	MJ
Erosion Resistance [Occupation]	3.07E-03	kg
Erosion Resistance [Transformation]	4.95E-06	kg/a
Feldspar (aluminium silicates) [Non renewable resources]	5.69E-17	kg
Ferro manganese [Non renewable resources]	2.30E-09	kg
Fluorspar (calcium fluoride; fluorite) [Non renewable resources]	3.84E-06	kg
GLO: sodium methoxide, at plant [organics]	7.00E-02	kg
Gold [Non renewable elements]	2.56E-10	kg
Granite [Non renewable resources]	1.05E-16	kg
Graphite [Non renewable resources]	2.10E-10	kg
Groundwater Replenishment [Transformation]	3.10E-03	(mm*m2)/a
Gypsum (natural gypsum) [Non renewable resources]	3.48E-04	kg
Hard coal (in MJ) [Hard coal (resource)]	3.43E+01	MJ
Hard coal USA [Hard coal, at production]	3.70E+00	kg

Table A3. (continued)

Structural bio-adhesive	Amount	Unit
Heavy spar (BaSO4) [Non renewable resources]	1.08E-06	kg
Hydrogen [Inorganic intermediate products]	1.32E-06	kg
Ilmenite (titanium ore) [Non renewable resources]	3.98E-07	kg
Industrial waste (incineration) [Waste for recovery]	1.40E-04	MJ
Inert rock [Non renewable resources]	7.39E+00	kg
Iridium [Non renewable elements]	2.75E-13	kg
Iron [Non renewable elements]	4.59E-03	kg
Kaolin ore [Non renewable resources]	6.26E-08	kg
Land Occupation [Occupation]	4.19E-02	m2
Land Transformation [Transformation]	4.20E-02	sqm
Lead [Non renewable elements]	4.05E-05	kg
Lignite (in kg) [Lignite (resource)]	3.87E-08	kg
Lignite (in MJ) [Lignite (resource)]	1.05E+00	MJ
Lime quicklime (lumpy) [Minerals]	2.07E-03	kg
Limestone (calcium carbonate) [Non renewable resources]	2.88E+00	kg
Magnesit (Magnesium carbonate) [Non renewable resources]	2.57E-05	kg
Magnesium chloride leach (40%) [Non renewable resources]	1.86E-04	kg
Manganese [Non renewable elements]	7.78E-05	kg
Mechanical Filtration [Occupation]	1.29E+01	cm
Mercury [Non renewable elements]	1.13E-10	kg
Molybdenum [Non renewable elements]	4.71E-06	kg
Municipal waste [Consumer waste]	3.95E-05	kg
Natural Aggregate [Non renewable resources]	1.12E-01	kg
Natural gas (in kg) [Natural gas (resource)]	9.60E-03	kg
Natural gas (in MJ) [Natural gas (resource)]	1.74E+01	MJ
Natural gas USA [Natural gas (resource)]	5.97E-01	kg
Natural pumice [Non renewable resources]	6.65E-06	kg
Nitrogen [Renewable resources]	1.11E-03	kg
Nuclear energy [Uranium (resource)]	2.89E-02	MJ
Occup. as Convent. arable land [Hemeroby]	1.14E-02	m2
Occupation, arable, conservation tillage [Hemeroby]	3.61E+01	sqm
Occupation, arable, conventional tillage [Hemeroby]	1.51E+01	sqm
Occupation, arable, reduced tillage [Hemeroby]	1.29E+01	sqm
Oil sand (10% bitumen) (in MJ) [Crude oil (resource)]	7.83E-03	MJ
Oil sand (100% bitumen) (in MJ) [Crude oil (resource)]	6.83E-03	MJ
Olivine [Non renewable resources]	2.37E-08	kg
Osmium [Non renewable elements]	3.35E-13	kg
Oxygen [Renewable resources]	3.31E-03	kg
PAG [Organic intermediate products]	0.99E+00	kg
Palladium [Non renewable elements]	4.87E-12	kg

Table A3. (continued)

Structural bio-adhesive	Amount	Unit
Peat (in kg) [Peat (resource)]	1.34E-06	kg
Peat (in MJ) [Peat (resource)]	1.58E-04	MJ
Phosphate ore [Non renewable resources]	3.11E-04	kg
Phosphorus [Non renewable elements]	1.38E-05	kg
Physicochemical Filtration [Occupation]	1.85E-02	(cmol*m2)/kg
Pit Methane (in MJ) [Natural gas (resource)]	3.07E-01	MJ
Platinum [Non renewable elements]	8.24E-12	kg
Potashsalt, crude (hard salt, 10% K2O) [Non renewable resources]	1.93E-03	kg
Potassium chloride [Inorganic intermediate products]	5.13E-05	kg
Potassium chloride [Non renewable resources]	8.38E-09	kg
Primary energy from geothermics [Renewable energy resources]	1.06E-03	MJ
Primary energy from hydro power [Renewable energy resources]	1.11E+01	MJ
Primary energy from solar energy [Renewable energy resources]	8.37E-01	MJ
Primary energy from waves [Renewable energy resources]	5.96E-06	MJ
Primary energy from wind power [Renewable energy resources]	3.12E-01	MJ
Primary forest [Renewable resources]	1.71E-07	kg
Pyrite [Non renewable resources]	1.84E-07	kg
Quartz sand (silica sand; silicon dioxide) [Non renewable resources]	1.86E-03	kg
Rhodium [Non renewable elements]	8.24E-13	kg
RNA: Bituminous coal, combusted in industrial boiler [Products and Intermediates]	2.46E-01	kg
RNA: Dummy, Disposal, solid waste, unspecified, to unspecified landfill [Dummy Flows]	2.63E-02	kg
RNA: Dummy, Heat, from biomiass [Dummy Flows]	1.91E-01	MJ
RNA: Dummy, Heat, from landfill gas [Dummy Flows]	9.55E-02	MJ
RNA: Dummy, Hexane, at plant [Dummy Flows]	8.95E-03	kg
RNA: Dummy_Agrochemicals, at plant [Dummy Flows]	8.24E-03	kg
RNA: Dummy_Electricity, at wind power plant, unspecified [Dummy Flows]	7.19E+00	MJ
RNA: Dummy_Phosphorous Fertilizer (TSP as P2O5), at plant [Dummy Flows]	7.92E-02	kg
RNA: Dummy_Potash Fertilizer (K2O), at plant [Dummy Flows]	1.47E-01	kg
RNA: Electricity, at grid, U.S. [Products and Intermediates]	3.14E+00	MJ
RNA: Electricity, at grid, US [Products and Intermediates]	1.43E+00	MJ
RNA: Transport, combination truck, diesel powered [Products and Intermediates]	5.11E+03	kgkm
RNA: Transport, single unit truck, diesel powered [Products and Intermediates]	3.48E-01	kgkm
RNA: Transport, train, diesel powered [Products and Intermediates]	3.30E+02	kgkm
Ruthenium [Non renewable elements]	1.62E-12	kg
Rutile (titanium ore) [Non renewable resources]	6.97E-35	kg
Sand [Non renewable resources]	3.33E-05	kg

Table A3. (continued)

Structural bio-adhesive	Amount	Unit
Shale [Non renewable resources]	3.48E-05	kg
Shale gas (in MJ) [Natural gas (resource)]	2.41E+00	MJ
Silver [Non renewable elements]	6.14E-08	kg
Slate [Non renewable resources]	1.29E-07	kg
Sodium chloride (rock salt) [Non renewable resources]	1.57E-02	kg
Sodium hydroxide (100%; caustic soda) [Inorganic intermediate products]	7.33E-02	kg
Sodium nitrate [Non renewable resources]	9.10E-18	kg
Sodium sulphate [Non renewable resources]	5.90E-14	kg
Soil [Non renewable resources]	1.41E-01	kg
Stone from mountains [Non renewable resources]	5.56E-04	kg
Sulphur (bonded) [Non renewable resources]	4.99E-11	kg
Sulphur [Non renewable elements]	4.46E-02	kg
Talc [Non renewable resources]	2.09E-09	kg
Tantalum [Non renewable elements]	6.71E-10	kg
Tight gas (in MJ) [Natural gas (resource)]	2.11E+00	MJ
Tin [Non renewable elements]	5.76E-19	kg
Tin ore [Non renewable resources]	2.41E-07	kg
Titanium [Non renewable elements]	9.61E-09	kg
Titanium ore [Non renewable resources]	4.64E-09	kg
Uranium natural (in MJ) [Uranium (resource)]	7.79E-01	MJ
Uranium oxide (U3O8), 332 GJ per kg, in ore [Uranium (resource)]	1.75E-05	kg
US: Bituminous coal, combusted in industrial boiler [Products and Intermediates]	2.58E-01	kg
US: Diesel, combusted in industrial boiler [Products and Intermediates]	7.55E-08	m3
US: Dummy_Disposal, ash and flue gas desulfurization sludge, to unspecified reuse [Dummy Flows]	1.18E-01	kg
US: Dummy_Disposal, chemical waste, unspecified, to sanitary landfill [Dummy Flows]	2.28E-06	kg
US: Dummy_Disposal, inert solid waste, to inert material landfill [Dummy Flows]	2.28E-06	kg
US: Dummy_Disposal, solid waste, unspecified, to sanitary landfill [Dummy Flows]	1.19E-02	kg
US: Dummy_Disposal, solid waste, unspecified, to unspecified landfill [Dummy Flows]	4.22E-07	kg
US: Dummy_Disposal, solid waste, unspecified, to unspecified treatment [Dummy Flows]	4.31E-01	kg
US: Dummy_Electricity, geothermal, unspecified [Dummy Flows]	5.73E-01	MJ
US: Dummy_Energy, unspecified [Dummy Flows]	1.85E-02	MJ
US: Dummy_Transport, pipeline, coal slurry [Dummy Flows]	1.86E+01	kgkm
US: Dummy_Transport, pipeline, natural gas [Dummy Flows]	9.47E+01	kgkm
US: Dummy_Transport, pipeline, unspecified [Dummy Flows]	6.19E+02	kgkm
US: electricity, production mix photovoltaic, at plant [power plants]	1.02E+00	MJ
US: Gasoline, combusted in equipment [Products and Intermediates]	1.06E-09	m3

Table A3. (continued)

Structural bio-adhesive	Amount	Unit
US: Liquefied petroleum gas, at refinery [Products and Intermediates]	1.38E-05	m3
US: Natural gas, combusted in industrial boiler [Products and Intermediates]	1.12E-02	m3
US: Residual fuel oil, combusted in industrial boiler [Products and Intermediates]	5.69E-06	m3
US: Transport, barge, average fuel mix [Products and Intermediates]	5.14E+02	kgkm
US: Transport, combination truck, average fuel mix [Products and Intermediates]	1.07E+02	kgkm
US: Transport, combination truck, diesel powered [Products and Intermediates]	1.46E+02	kgkm
US: Transport, ocean freighter, average fuel mix [Products and Intermediates]	6.27E+02	kgkm
US: Transport, ocean freighter, diesel powered [Products and Intermediates]	1.27E+01	kgkm
US: Transport, ocean freighter, residual fuel oil powered [Products and Intermediates]	1.14E+02	kgkm
US: Transport, train, diesel powered [Products and Intermediates]	3.93E+03	kgkm
Vanadium [Non renewable elements]	3.53E-08	kg
Water (feed water) [Water]	4.20E-02	kg
Water (ground water) [Water]	1.09E+01	kg
Water (lake water) [Water]	2.79E+03	kg
Water (rain water) [Water]	2.93E+00	kg
Water (river water) [Water]	1.06E+04	kg
Water (sea water) [Water]	4.52E+01	kg
Water (well water) [Water]	5.50E+02	kg
Water [Water]	1.43E+00	kg
Zinc [Non renewable elements]	3.82E-05	kg
Zirconium [Non renewable elements]	6.93E-14	kg

Table A4 Pressure sensitive bio-adhesive (PSA) modeled in GaBi.

PSA	Amount	Unit
Acrylated Acid [Organic intermediate products]	1	kg
AIBN [Organic intermediate products]	4.92E-05	kg
Air [Renewable resources]	2.95E+01	kg
Antimony [Non renewable elements]	3.63E-10	kg
Barium sulphate [Non renewable resources]	2.47E-15	kg
Basalt [Non renewable resources]	1.13E-07	kg
Bauxite [Inorganic intermediate products]	1. 21E-01	kg
Bauxite [Non renewable resources]	1.12E-04	kg
Bentonite [Non renewable resources]	1.74E-03	kg
Biomass (solid) [Biomass fuels]	2.23E-07	kg
Biotic Production [Occupation]	2.02E-02	kg
Biotic Production [Transformation]	1.69E-04	kg/a
Calcium chloride [Non renewable resources]	2.53E-13	kg
Carbon dioxide [Renewable resources]	4.94E-01	kg
Carcass meal [Hazardous waste for recovery]	1.03E-15	kg
Chromium [Non renewable elements]	4.35E-05	kg
Clay [Non renewable resources]	1.21E-03	kg
Coalbed methane (in MJ) [Natural gas (resource)]	5.56E-01	MJ
Cobalt [Non renewable elements]	1.49E-10	kg
Colemanite ore [Non renewable resources]	1.15E-06	kg
Copper [Non renewable elements]	1.65E-04	kg
Crude oil (in kg) [Crude oil (resource)]	1.38E-01	kg
Crude oil (in MJ) [Crude oil (resource)]	1.62E+01	MJ
Diesel [Refinery products]	1.69E-01	kg
Dolomite [Non renewable resources]	1.37E-04	kg
Electricity (product) [Electric power]	5.23E+01	MJ
Electricity [Electric power]	6.21E-01	MJ
Erosion Resistance [Occupation]	3.07E-03	kg
Erosion Resistance [Transformation]	5.01E-06	kg/a
Feldspar (aluminium silicates) [Non renewable resources]	1.48E-19	kg
Ferro manganese [Non renewable resources]	5.76E-12	kg
Fluorspar (calcium fluoride; fluorite) [Non renewable resources]	3.75E-06	kg
GLO: sodium methoxide, at plant [organics]	7.07E-02	kg
Gold [Non renewable elements]	2.54E-10	kg
Granite [Non renewable resources]	2.76E-19	kg
Graphite [Non renewable resources]	2.08E-10	kg
Groundwater Replenishment [Transformation]	3.10E-03	(mm*m2)/a
Gypsum (natural gypsum) [Non renewable resources]	3.51E-04	kg
Hard coal (in MJ) [Hard coal (resource)]	3.46E+01	MJ
Hard coal USA [Hard coal, at production]	3.74E+00	kg

Table A4. (continued)

PSA	Amount	Unit
Heavy spar (BaSO4) [Non renewable resources]	6.73E-08	kg
Hydrogen [Inorganic intermediate products]	3.46E-09	kg
Ilmenite (titanium ore) [Non renewable resources]	4.01E-07	kg
Industrial waste (incineration) [Waste for recovery]	3.87E-07	MJ
Inert rock [Non renewable resources]	7.42E+00	kg
Iridium [Non renewable elements]	2.76E-13	kg
Iron [Non renewable elements]	4.63E-03	kg
Kaolin ore [Non renewable resources]	6.19E-08	kg
Land Occupation [Occupation]	4.18E-02	m2
Land Transformation [Transformation]	4.18E-02	sqm
Lead [Non renewable elements]	4.08E-05	kg
Lignite (in kg) [Lignite (resource)]	9.56E-11	kg
Lignite (in MJ) [Lignite (resource)]	1.03E+00	MJ
Lime quicklime (lumpy) [Minerals]	2.09E-03	kg
Limestone (calcium carbonate) [Non renewable resources]	2.91E+00	kg
Magnesit (Magnesium carbonate) [Non renewable resources]	2.57E-05	kg
Magnesium chloride leach (40%) [Non renewable resources]	1.83E-04	kg
Manganese [Non renewable elements]	7.84E-05	kg
Mechanical Filtration [Occupation]	1.28E+01	cm
Mercury [Non renewable elements]	3.09E-13	kg
Molybdenum [Non renewable elements]	4.75E-06	kg
Municipal waste [Consumer waste]	1.05E-07	kg
Natural Aggregate [Non renewable resources]	1.13E-01	kg
Natural gas (in kg) [Natural gas (resource)]	2.56E-05	kg
Natural gas (in MJ) [Natural gas (resource)]	1.75E+01	MJ
Natural gas USA [Natural gas (resource)]	6.03E-01	kg
Natural pumice [Non renewable resources]	6.71E-06	kg
Nitrogen [Renewable resources]	2.79E-06	kg
Nuclear energy [Uranium (resource)]	8.80E-05	MJ
Occup. as Convent. arable land [Hemeroby]	1.13E-02	m2
Occupation, arable, conservation tillage [Hemeroby]	3.65E+01	sqm
Occupation, arable, conventional tillage [Hemeroby]	1.53E+01	sqm
Occupation, arable, reduced tillage [Hemeroby]	1.30E+01	sqm
Oil sand (10% bitumen) (in MJ) [Crude oil (resource)]	7.88E-03	MJ
Oil sand (100% bitumen) (in MJ) [Crude oil (resource)]	6.89E-03	MJ
Olivine [Non renewable resources]	5.94E-11	kg
Osmium [Non renewable elements]	3.36E-13	kg
OXCART [Organic intermediate products]	1.45E-04	kg
Oxygen [Renewable resources]	3.14E-03	kg
Palladium [Non renewable elements]	4.88E-12	kg

Table A4. (continued)

PSA	Amount	Unit
Peat (in kg) [Peat (resource)]	6.02E-08	kg
Peat (in MJ) [Peat (resource)]	1.56E-04	MJ
Phosphate ore [Non renewable resources]	3.12E-04	kg
Phosphorus [Non renewable elements]	4.70E-06	kg
Physicochemical Filtration [Occupation]	1.83E-02	(cmol*m2*a)/kg
Pit Methane (in MJ) [Natural gas (resource)]	3.09E-01	MJ
Platinum [Non renewable elements]	8.26E-12	kg
Potashsalt, crude (hard salt, 10% K2O) [Non renewable resources]	1.93E-03	kg
Potassium chloride [Inorganic intermediate products]	5.18E-05	kg
Potassium chloride [Non renewable resources]	2.14E-11	kg
Primary energy from geothermics [Renewable energy resources]	1.04E-03	MJ
Primary energy from hydro power [Renewable energy resources]	1.12E+01	MJ
Primary energy from solar energy [Renewable energy resources]	8.26E-01	MJ
Primary energy from waves [Renewable energy resources]	1.97E-08	MJ
Primary energy from wind power [Renewable energy resources]	3.08E-01	MJ
Primary forest [Renewable resources]	4.80E-10	kg
Pyrite [Non renewable resources]	1.85E-07	kg
Quartz sand (silica sand; silicon dioxide) [Non renewable resources]	1.86E-03	kg
Rhodium [Non renewable elements]	8.27E-13	kg
RNA: Bituminous coal, combusted in industrial boiler [Products and Intermediates]	2.49E-01	kg
RNA: Dummy, Disposal, solid waste, unspecified, to unspecified landfill [Dummy Flows]	2.66E-02	kg
RNA: Dummy, Heat, from biomiass [Dummy Flows]	1.93E-01	MJ
RNA: Dummy, Heat, from landfill gas [Dummy Flows]	9.65E-02	MJ
RNA: Dummy, Hexane, at plant [Dummy Flows]	9.04E-03	kg
RNA: Dummy_Agrochemicals, at plant [Dummy Flows]	8.32E-03	kg
RNA: Dummy_Electricity, at wind power plant, unspecified [Dummy Flows]	7.27E+00	MJ
RNA: Dummy_Phosphorous Fertilizer (TSP as P2O5), at plant [Dummy Flows]	8.00E-02	kg
RNA: Dummy_Potash Fertilizer (K2O), at plant [Dummy Flows]	1.49E-01	kg
RNA: Electricity, at grid, U.S. [Products and Intermediates]	3.18E+00	MJ
RNA: Electricity, at grid, US [Products and Intermediates]	1.44E+00	MJ
RNA: Transport, combination truck, diesel powered [Products and Intermediates]	5.16E+03	kgkm
RNA: Transport, single unit truck, diesel powered [Products and Intermediates]	3.52E-01	kgkm
RNA: Transport, train, diesel powered [Products and Intermediates]	3.34E+02	kgkm
Ruthenium [Non renewable elements]	1.63E-12	kg
Rutile (titanium ore) [Non renewable resources]	1.73E-37	kg
Sand [Non renewable resources]	8.34E-08	kg

Table A4. (continued)

PSA	Amount	Unit
Shale [Non renewable resources]	3.52E-05	kg
Shale gas (in MJ) [Natural gas (resource)]	2.44E+00	MJ
Silver [Non renewable elements]	6.15E-08	kg
Slate [Non renewable resources]	3.18E-10	kg
Sodium chloride (rock salt) [Non renewable resources]	1.19E-02	kg
Sodium hydroxide (100%; caustic soda) [Inorganic intermediate products]	7.40E-02	kg
Sodium nitrate [Non renewable resources]	2.23E-20	kg
Sodium sulphate [Non renewable resources]	5.95E-14	kg
Soil [Non renewable resources]	1.42E-01	kg
Steam (MJ) [steam]	3.49E-03	MJ
Stone from mountains [Non renewable resources]	4.30E-04	kg
Sulphur (bonded) [Non renewable resources]	1.25E-13	kg
Sulphur [Non renewable elements]	4.50E-02	kg
Talc [Non renewable resources]	2.07E-09	kg
Tantalum [Non renewable elements]	6.62E-10	kg
Tight gas (in MJ) [Natural gas (resource)]	2.13E+00	MJ
Tin [Non renewable elements]	5.79E-19	kg
Tin ore [Non renewable resources]	2.37E-07	kg
Titanium [Non renewable elements]	9.53E-09	kg
Titanium ore [Non renewable resources]	4.57E-09	kg
Uranium natural (in MJ) [Uranium (resource)]	7.69E-01	MJ
Uranium oxide (U3O8), 332 GJ per kg, in ore [Uranium (resource)]	1.77E-05	kg
US: Bituminous coal, combusted in industrial boiler [Products and Intermediates]	2.60E-01	kg
US: Diesel, combusted in industrial boiler [Products and Intermediates]	7.62E-08	m3
US: Dummy_Disposal, ash and flue gas desulfurization sludge, to unspecified reuse [Dummy Flows]	1.20E-01	kg
US: Dummy_Disposal, chemical waste, unspecified, to sanitary landfill [Dummy Flows]	2.30E-06	kg
US: Dummy_Disposal, inert solid waste, to inert material landfill [Dummy Flows]	2.30E-06	kg
US: Dummy_Disposal, solid waste, unspecified, to sanitary landfill [Dummy Flows]	1.20E-02	kg
US: Dummy_Disposal, solid waste, unspecified, to unspecified landfill [Dummy Flows]	1.04E-09	kg
US: Dummy_Disposal, solid waste, unspecified, to unspecified treatment [Dummy Flows]	4.35E-01	kg
US: Dummy_Electricity, geothermal, unspecified [Dummy Flows]	5.79E-01	MJ
US: Dummy_Energy, unspecified [Dummy Flows]	1.87E-02	MJ
US: Dummy_Transport, pipeline, coal slurry [Dummy Flows]	1.88E+01	kgkm
US: Dummy_Transport, pipeline, natural gas [Dummy Flows]	9.47E+01	kgkm
US: Dummy_Transport, pipeline, unspecified [Dummy Flows]	6.26E+02	kgkm

Table A4. (continued)

PSA	Amount	Unit
US: electricity, production mix photovoltaic, at plant [power plants]	1.03E+00	MJ
US: Gasoline, combusted in equipment [Products and Intermediates]	1.07E-09	m3
US: Liquefied petroleum gas, at refinery [Products and Intermediates]	1.40E-05	m3
US: Natural gas, combusted in industrial boiler [Products and Intermediates]	1.03E-02	m3
US: Residual fuel oil, combusted in industrial boiler [Products and Intermediates]	5.75E-06	m3
US: Transport, barge, average fuel mix [Products and Intermediates]	5.19E+02	kgkm
US: Transport, combination truck, average fuel mix [Products and Intermediates]	1.08E+02	kgkm
US: Transport, combination truck, diesel powered [Products and Intermediates]	1.47E+02	kgkm
US: Transport, ocean freighter, average fuel mix [Products and Intermediates]	6.33E+02	kgkm
US: Transport, ocean freighter, diesel powered [Products and Intermediates]	1.28E+01	kgkm
US: Transport, ocean freighter, residual fuel oil powered [Products and Intermediates]	1.15E+02	kgkm
US: Transport, train, diesel powered [Products and Intermediates]	3.97E+03	kgkm
Vanadium [Non renewable elements]	3.48E-08	kg
Water (feed water) [Water]	1.10E-04	kg
Water (ground water) [Water]	1.10E+01	kg
Water (lake water) [Water]	2.82E+03	kg
Water (rain water) [Water]	2.91E+00	kg
Water (river water) [Water]	1.07E+04	kg
Water (sea water) [Water]	4.56E+01	kg
Water (well water) [Water]	5.55E+02	kg
Water [Water]	1.05E+00	kg
Zinc [Non renewable elements]	3.82E-05	kg
Zirconium [Non renewable elements]	6.83E-14	kg